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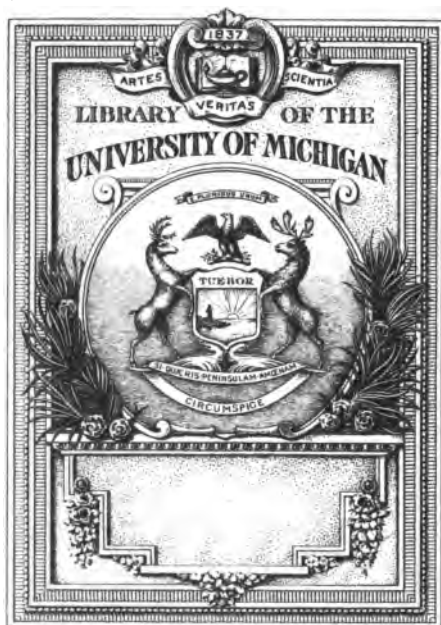
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# **EVERYMAN'S CHEMISTRY**



**HARPER'S MODERN SCIENCE SERIES**

# **EVERYMAN'S CHEMISTRY**

**THE CHEMIST'S POINT OF VIEW  
AND HIS RECENT WORK  
TOLD FOR THE LAYMAN**

**BY  
ELLWOOD HENDRICK**



**HARPER & BROTHERS PUBLISHERS  
NEW YORK AND LONDON**

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### EVERYMAN'S CHEMISTRY

The Chemist's Point of View and His Present Work

By ELLWOOD HENDRICK

(Other Volumes in Preparation)

HARPER & BROTHERS, NEW YORK

[ESTABLISHED 1817]

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## PREFACE

THE second decade of the twentieth century has brought to the average man a general, if vague, realization of the tremendous importance of chemistry and its application in actual life. I think this has never been felt so acutely before, and yet it has seemed to me that the same average man is not very well provided with a work that he could read and understand easily and at the same time get a chemical view of things. To produce such a book has been my purpose, and if I have not made it interesting I shall be to blame, for I assure you the subject is full of interest and delight. Of course this is not a complete treatise on chemistry, nor do I pretend that it is a well-balanced book. Many important subjects are touched upon but lightly, and others of less general value I have not hesitated to ramble on about at considerable length, so long as they seemed interesting. The whole thing is, in a way, a sporting proposition between you, the reader, and me. If I can hold your attention until you have read it through, I shall have succeeded in my undertaking and you will know something about the Ways of Stuff as the chemist has to do with them. You will be out of the inky darkness. You will not think that a barrel of coal-tar, for instance, put into a pot and boiled with a teacupful of one thing and a tablespoonful of t'other will straightway resolve itself into dyestuffs, perfumes,

## PREFACE

medicines, and what not, according to the will of the man with the thermometer. You will not know how the chemist works so much as you will of the way he thinks; and instead of presenting him to you as a superman with potentialities and powers beyond his kind, I have tried to make it clear that his problems are very like those of a business man. The difference is that the man of affairs deals with others of his kind whose minds are hidden from him, trying to induce them to do his bidding, whereas the chemist deals with molecules and atoms and ions, none of which he can see, but which also have ways of their own that are often exceedingly difficult to master. My only stipulation is that you shall not attempt to read the book backward. And yet I pray you to refer frequently to the table of elements at the end. It contains information that you will find useful as you read along, and I should have put it at the beginning had I not feared that it would frighten you away.

Chemistry would be the dullest study on earth if it only had to do with the proportionate amounts of oxygen, nitrogen, sulphur, etc., that a body contains. This is merely the genealogy of things, and bears the same relation to them that the names of a man's several grandparents do to him. The interest lies in what these things will do, just as the interesting quality of a man lies in the problem of what he will do under more or less known conditions.

For those who desire to read more profoundly I have added a select bibliography of standard works, some of which are easy to read and some of which are written with the understanding that the reader shall have devoted several years to the study of the subjects treated. This appears in an appendix.

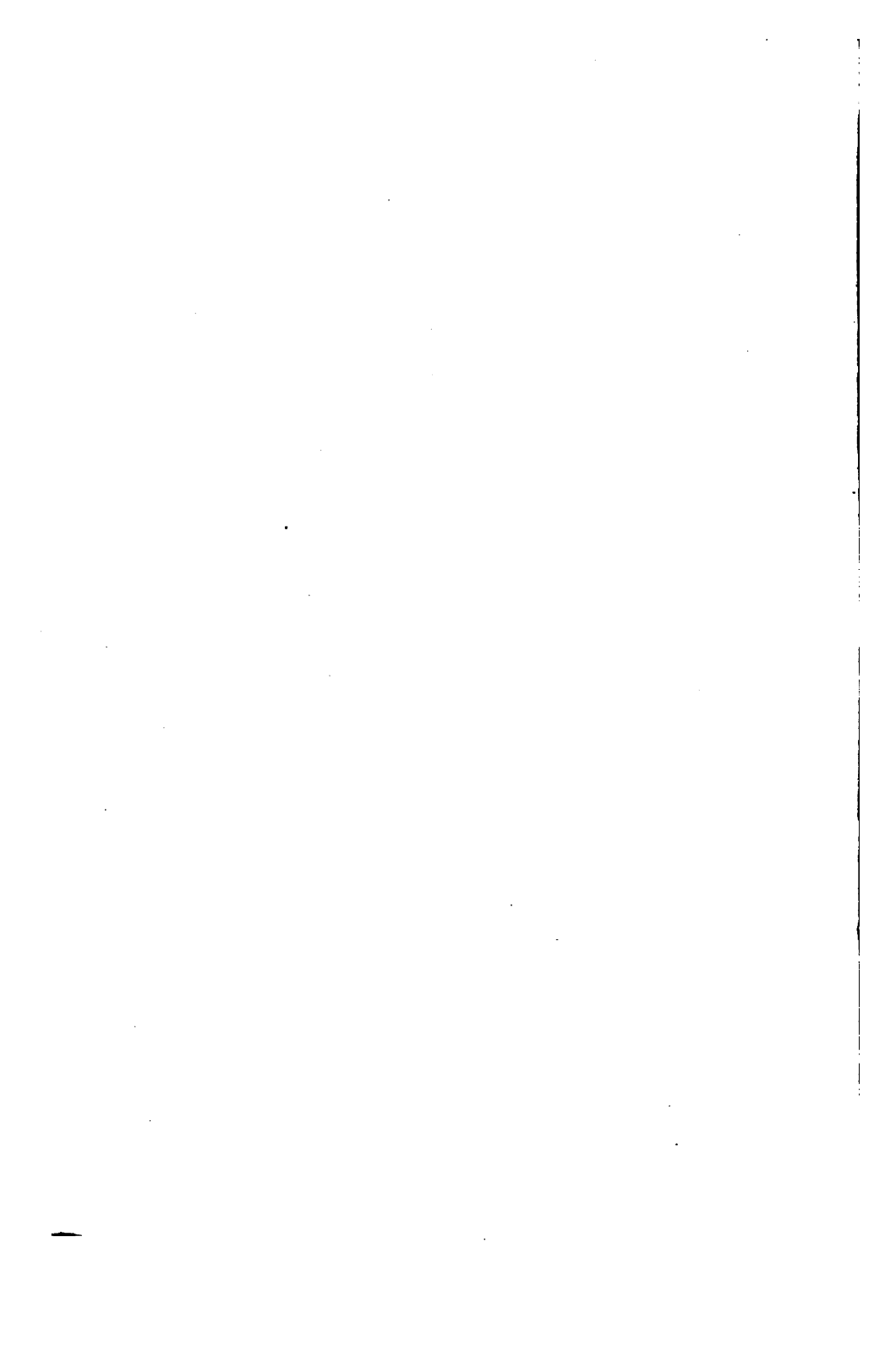


## P R E F A C E

I am indebted to more friends than I can name for information. I have consulted with many who are actively engaged in special work in chemistry as to the status of various industries. I spent some time at the Mellon Institute of Industrial Research, of the University of Pittsburgh, and, thanks to Dr. Raymond F. Bacon, the Director, and many of the Fellows of the Institute, I have been able to indicate the developments of some subjects that would not otherwise have been available to me. Prof. William A. Hamor, Assistant Director of the Institute, has set aside work of pressing importance to go over most of the manuscript and make suggestions. The faults are all mine, but many of the merits of the book, if it should prove to have them, are the result of his encyclopedic knowledge of chemical literature. In fact, the way in which my chemist friends offered their aid as soon as I told them what I was about to do has made me not only very grateful, but has impressed upon me the need of just such a book as I have tried to write. I offer my hearty thanks to them all, and I bid you, in all modesty, to enter with me into what has been called that branch of philosophy and poetry which has to do with the Ways of Stuff.

E. H.

139 EAST 40th STREET, NEW YORK,  
*June, 1917.*



**PART FIRST**  
**GENERAL AND INTRODUCTORY**



# EVERYMAN'S CHEMISTRY

## I

### CHEMICAL MISERIES

The Troubles of Neighbor Robinson—The Value of Chemical Advice and the Need of Chemical Control—The Legend of the Dunderhead Manufacturing Company—"All the Chemistry We Need"—Inventors and Their Ways—The Intelligence Department of Industry

LET us consider the man on the street—not the one leaning against a lamp-post, but a man of circumstance going about his affairs—as meeting a friend and walking along with him. After the usual preliminary greetings, the following conversation might ensue:

"How is Robinson?"

"I am afraid Robinson has pneumonia."

Then we know what would follow. They would discuss questions of diet, Robinson's habits of life and his age, the peculiarities of the disease, the publications of medical research as recorded in the newspapers, and they would talk as two intelligent men would talk about a frequently occurring disease. They are not physicians, but they have a lay understanding of the professional life of the physician and the manner in which he meets his problems. And they consider

## EVERYMAN'S CHEMISTRY

Robinson's chances of recovery. A similar discussion would follow the announcement, had it been made, that Robinson had neuritis, peritonitis, appendicitis, locomotor ataxia, or any of a score of other diseases with names having Latin and Greek entanglements.

In other words, medicine has broken into society and it is an interesting subject of the talk of intelligent laity in their hours of leisure.

Now let us imagine that Robinson is whole in body, but is having business troubles. He is a wholesale druggist and has been spending a great deal of money in advertising Robinson's Liquid Petrolatum, which is sold as medicine. Then the conversation might take this turn:

"How is Robinson?"

"He is in a bad way."

"Is he ill?"

"No; it is business. You know that petroleum product he has been advertising?"

"Yes; I thought it was a gold-mine."

"Not exactly that, although it is an excellent thing, but something has gone wrong and the stuff is coming back to him by the car-load. Smells like kerosene and people don't like the taste of it."

"What is the matter with it?"

"They say it is olefins." (In point of fact it might be due to other bodies, but the expression is convenient; let's use it.)

"Ole Fins? Who's he? Is he a Swede?"

"No; olefins are some kind of unsaturated hydrocarbons and—"

"Never mind. I don't know anything about chemistry."

"Neither do I, and I'm glad I don't have anything to do with it. You never know where you are with

## CHEMICAL MISERIES

chemical products. Here's poor Robinson, who works up a nice business with that petroleum stuff of his and then for no reason at all it goes back on him."

"That's right. I'm sorry for Robinson."

Now the first chapter of a book is, in effect, an advertisement, designed to lure the reader on into a diligent perusal of what follows. Sugar-coat the pill as we may, that is the problem of an author. He must, if he can, lure the reader on. So, proceeding as though this were printed in large, bold-face type and adorned with illustrations supposed to be convincing, I ask you to look upon the discussion of the troubles of Robinson, which I have just indicated, as typical of the conversation of two intelligent *laymen who have not read this book*. Permit me, then, to indicate, in a few more imaginary conversations between the same gentlemen, types of their intercourse *after reading*. Repeat, if you will, the same talk, beginning with "How is Robinson?" until the point is reached where olefins are supposed to constitute a Swede. Now observe the change:

"Olefins?"

"Yes; unsaturated hydrocarbons, you know."

"Can't they be separated?"

"I believe they can. Trouble with Robinson is, I'm afraid, he is a little too anxious to make money. The United States Bureau of Mines has been turning out many papers on petroleum, and I understand that at Columbia University and at the Mellon Institute in Pittsburgh they have been making researches for years. Just as likely as not the information that Robinson needs has been published already."

"Maybe he didn't know there were olefines in his stuff."

"Well, he ought to, and if that is not his trouble he

## EVERYMAN'S CHEMISTRY

ought to know what is. What he did, probably, was to start with some oil that was pretty clean, and then when he ran through a new lot the agony began. Robinson is one of those who think that if they have a formula for making something, any old raw material will do. He was born about forty years too late to manufacture that way. Why didn't he take advice? I'm sorry for him, but I hope this will make him mend his ways."

This criticism might not be pleasant for Robinson, but it might be better for him than sympathy. Let us now make believe that Brown, another friend, is having trouble because his sheds, which were covered with steel sheeting, have rusted so that he is using up a lot of his profits in repairs. Then the talk might take this turn:

"Where did he get his steel?"

"He doesn't know; the contractor bought it."

"Didn't he specify that he wanted copper alloyed with it?"

"No; he only specified the gauge."

"Just think of that! Only a little copper in the steel, a quarter of one per cent., might have made it last years and years instead of no time at all. I'm sorry for Brown, but he is getting just what happens to men who think a practical man must know everything. Brown should study, or, better still, seek advice."

This information is not to be found in this book alone. It is published elsewhere in much greater detail. There is not a single discovery here set forth and published for the first time to a supposedly awe-inspired world. What I am trying to do is to treat of innate matter, not as though it were dead, but rather as having within it, as it has, constant potentialities



## CHEMICAL MISERIES

of action. Matter does not act and react according to a few fixed rules; there are rules by the hundred, and we shall not attempt to repeat them. Then, too, time and again, to all intents and purposes, they seem to be broken. There are certain general principles, however, which seem to hold good, just as certain general principles seem to hold good in dealing with men. Some of these I shall try to indicate as we proceed. Every subject mentioned is a study in itself, and concerning which, in many cases, whole libraries have been written.

If you want chemical advice, remember that nobody living knows all there is of chemistry, but that some men are remarkably well informed on certain subjects. How to find the man you need is an undeveloped art, but a good thing to do is to get acquainted with a sound chemist and consult him or talk with him about your business affairs. It is surprising into how many places, if he is a sound man, he will be able to throw light. It may interest you to know that the Bureau of Employment of the Chemists' Club of New York maintains an excellent list of consultants and chemical engineers as well as of chemists who seek employment. The editors of the *Journal of Industrial and Engineering Chemistry* of the American Chemical Society and of *Metallurgical and Chemical Engineering* are remarkably well posted as to men. Being sincerely interested in the development of American industrial chemistry, they are glad of the opportunity to help.

The time is soon coming when manufacturing establishments will need a chemist in consultation just as much as they need a lawyer now. If they are negotiating with customers or with other corporations, they need a lawyer to draw their contracts and see that they do not make mistakes. Well, if they are nego-

## EVERYMAN'S CHEMISTRY

tiating with materials, they need a chemist, for chemistry treats of the ways of stuff, and these are full of unexpected turnings. Chemical control is needed.

This is bound to come, but it hasn't arrived yet. And when it does come, there are sure to be comedies enacted in relation to it, and very expensive comedies withal. Now the truth, as you are likely to read more than once in this book, is all the facts arrayed in their right relation, which is why we do not always succeed in telling it, no matter how hard we try. Teaching by parable is an old and tried method, and, in order to bring out the need of a competent chemist in counsel, let us imagine a story. Before we begin, however, please remember that chemistry is a very broad subject, like farming. In that profession one man is good at raising cattle, another breeds horses, another is a great expert in vegetables, while others are good all-round men who do not profess to know everything, but have the knack of getting needed information and finding the best authorities. These men are likely to succeed as consultants, and of such I beg you to consider Doctor Noyadont, who will shortly appear.

Now let us suppose a meeting of the board of the Dunderhead Manufacturing Co., and that, in order to conform to the prospective fashion of having a chemist in counsel, the directors have filled a vacancy by electing young Brown, who is engaged in testing materials in their cupboard of a laboratory somewhere under a stairway. Then suppose the most affluent, the most pompous, the vainest if not the richest director, the father-in-law of the secretary of the Sand & Stone Co., were to offer the following motion: "*Resolved*, That, prices being equal, this corporation shall purchase its rock from the Sand & Stone Co."

## CHEMICAL MISERIES

The young chemist apologizes for speaking, and says that Sand & Stone are agents for Blue Mountain rock, and that this rock seemed to show traces of dubium, which he fears might give trouble in the works.

"Whatcha mean?" roars the affluent one to the pale B.S.

"Well, I—er—it doesn't seem to me that it works as well as the Earth & Rock Co.'s product that I believe comes from Green Mountain. I thought I found traces of dubium there, and, you know, there might be a catalytic effect—"

"Cataclysmic effect," exclaims the old heavyweight. "Young man, is that what you think or what you guess?"

"Why, I'm not sure, but I think—"

"That's what you think, is it? Well, sir, when you know something let's hear from you, but we don't care for any of your guesses. The Sand & Stone Co. are the largest dealers in this material in the world, and if I tell them to send us rock without any of this here dubium in it, they'll send it. I call for my motion, Mr. Chairman."

The motion is put and carried.

In one year's time the asset of the corporation's name as a trade-mark becomes a liability; they cannot persuade people that their product is not tainted. Even after they have seen the folly of their ways and given up the use of Blue Mountain rock and turn out a product better than ever before, their reputation is still bad.

"Better not buy of 'em," says one customer to a prospective one. "They tried to run off a lot of inferior material on me, but I made 'em take it back."

"One of their drummers was in not long ago and he said they had had a fault, but had corrected it;

## EVERYMAN'S CHEMISTRY

they had some sort of jubilee or other in the rock they make it of, but he says it's all right now."

"That's what they say. J'ver know a concern that wasn't all right when they wanted to make a sale?"

"That's so. Better be on the safe side," says Mr. Prospective Customer, and he buys from the rival company.

Now suppose, instead of electing the young chemist from the works, a consulting chemist of standing is selected, retained and added to the board to avoid mistakes *at the start*, which is the Grand Economy. Let us imagine the same corporation, same chairman and president, same pompous old party with a son-in-law with Sand & Stone, same general counsel, and the same other members, except that Doctor Noyadont of the Noyadont Laboratories sits in the place of young Brown, the chemist at the works. Unlike Brown, Doctor Noyadont has not bought himself a house in the neighborhood of the factory, and has not married on the prospects of the good-will of the very board of which he is a member. Doctor Noyadont likes his annual retainer, which may be more than Brown's salary, but he does not live on it. Then let us imagine the same proposal of the affluent Mr. Fatwad that the corporation procure its rock from Sand & Stone.

Doctor Noyadont speaks up: "Sorry, Mr. Fatwad, but I shall have to oppose that motion. I've examined the Blue Mountain rock that they handle, and it is not good for our purpose."

"Why not?"

"Appears to be dubium in it."

"But these people are the largest producers of rock in the world, and do you mean to tell me—?"

"I mean to tell you not to use any Blue Mountain

## CHEMICAL MISERIES

rock. It's the best there is for some purposes, but not for us."

Old Fatwad observes that Doctor Noyadont is neither afraid nor uncertain of his ground. But he likes to have his way, and he proposes a committee of three, including Doctor Noyadont, to ascertain.

"No occasion for me to look it up any more," says Doctor Noyadont. "Go ahead and buy all the Blue Mountain rock you want to," he continues, "but with it comes my resignation from the board and from the office of your consulting chemist. Mr. Fatwad expects your processes to move on all calm and serene in the presence of a catalytic agent that may start up all sorts of reactions that you don't want. I can't be sure of your product under those conditions. If some member of the board were to propose to break the laws of the State or the nation, your general counsel here would advise you against it, and if you were to persist in it he would resign. Well, here you propose to break nature's laws and expect to keep out of trouble after you've done it. I call for the question, Mr. Chairman, because it involves a matter about which we should not be in doubt for one minute. And I offer my resignation now to take effect as soon as the motion is carried."

Mr. Fatwad then withdraws his motion. He may see a light, and again he may not, but the chances are that he will, because he is nobody's fool. But rich men's vanity is one of the most difficult things to overcome. When it is quiescent it is invisible and harmless; when it is active it is hard to endure and highly dangerous. The only way to deal with it when it is active is to whack it on the head. No employee can do this without providing for himself first a good, safe runway into the tall timber.

## EVERYMAN'S CHEMISTRY

There should be a chemist on the board of every corporation that has to do with chemical processes. He should be a man of attainment, of distinction, and of backbone.

So much for imaginary conversations. But I could, if I had a mind, tell you true stories of real men that sound very like them. Let's content ourselves with a single one, drawn from life. It has to do with a great corporation that was in a bad way, especially troubled by the ruinous prices that "unprincipled" competitors were charging for wares. Later examination proved that they were wasting several hundred thousand dollars annually from not knowing what was actually taking place among the materials in their works. Their men were doing as they were told with diligence, but their materials were up to mischief. The man in authority replied to the suggestion that they have their plant examined by a competent chemical engineer that his boy was a sophomore at Yale and was taking up chemistry among his studies, "and so you see," he concluded, "we get all the chemistry we need."

This book is written for the man who shakes his head with the exclamation that he does not know anything about chemistry whenever the subject is mentioned. I have not the ignorant man in mind when I say this, but one whose peregrinations in the pathways of knowledge have not included the ways of so-called inanimate, but, in fact, very lively matter. To make things easy, I suggest that we take the point of view that matter, instead of being inert, has ways of its own, and likes and dislikes and foibles galore; in short, that it has personal qualities. This may not be taking the most exalted view of the processes of nature, and it is not the fashionable method of teach-

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ing, but it will be a workable view. We need not enter into the problem of whether the processes of life are wholly of a physico-chemical nature or not. We shall not study them profoundly or speculate upon them. So far as we are concerned and without growing too serious over it, let us go the most enthusiastic vitalists one better and, finding motion in the whirling atoms of the common stone, call everything alive. Even a dead mouse can make trouble.

Another thing that has bothered me like the voice of conscience while planning this work has been the way in which chemical undertakings are often organized—and then fail. Some inventor comes along with what seems like a good idea. Let's admit that it is a good idea. The inventor "knows all about chemistry," and he is also certain that other persons engaged in the effort to produce the same materials have not seen the great light that has been revealed to him. This great light may be as evident as that two and two make four, but the inventor believes himself the sole repository of the knowledge. These are danger signs, and would be to the wise manufacturer the signal to see a competent chemical engineer, get him to look up the literature, and then possibly make a trip somewhere and find out more about it. He need not give the secret away, although the chances are ten to one that a full account of the reactions is given somewhere in chemical literature. But let us imagine that the inventor is right, which is guessing against odds, and imagine the company formed to begin manufacture. How many chemical inventors are good engineers? They are few and far between. The tanks and machinery, the valves, pipes, filter presses, and what not must be ordered and installed, and we meet another chance for failure because of defective

## EVERYMAN'S CHEMISTRY

mechanical construction. But let us imagine the works to be well designed and the goods to be produced—not quite in measure and kind as expected—but produced. Then comes the problem of business administration, and here people fail again. A chemical enterprise needs just as much business ability to operate it as does any other. Why an otherwise unfortunate relative or friend out of a job should be regarded as the very man to undertake the business management of a new industry is hard to understand, but it is done time and again. It shows how hope springs eternal in the human breast, but it does not prove wisdom.

Now the thing to know first in manufacture is that a process is right, not only in glass in the laboratory, but under the entirely different conditions of mass and surface and pressure in iron in the works. That is the reason why it is so wise to build a test plant first and prove out every detail. The laboratory must keep on the track of the materials used and produced just as the accounting department must keep records of costs, and if things go wrong the chemical adviser should be called in, just as he was at the start, and just as the medical adviser is called in at the birth and on the occasion of sickness of a person.

Chemical manufacture is not always a difficult procedure. Many processes are by no means so involved as making shoes or hats or furniture—all of which have a chemical as well as a mechanical side. What is needed is a sense of what is going on inside of all the pots, kettles, boilers, and containers of one sort or another, and then the same requirements hold good that are demanded by other industries.

Of course, many manufacturers have their own



## CHEMICAL MISERIES

secret processes and chemical short-cuts that have great value to them, but it is a fair guess that, of chemical secrets, at least three-fourths of them are known and are of public record.

Chemistry is not only the intelligence department of industry; it is everywhere, and we cannot get away from it. Every kitchen is a laboratory, every baker is a chemical manufacturer, and every butcher is a chemical warehouseman. Chemistry washes us, launders our clothes, and bleaches and dyes them; it provides us with metals, with our morning paper, and with books; it helps the farmer to grow our food; and when all is over, whether we be burned to ashes or buried in the ground, it is by chemical processes that our bodies go back again into the great order of things.

## II

### THE HEART OF THE THING

The World beyond the Microscope—The Nature of Matter—Atoms and Molecules—Speculations—The Middle of the Road—The Law of Avogadro—No Such Thing as Rest—Polygamy in Chemistry—A Little Confidential Talk

THE world beyond the microscope is as vast as that beyond the telescope. We can see and feel a few things, just a few, within the very narrow range of our ken, and all the rest is beyond. We have to compute what we know or what seems likely about it. There is a kind of cousinship between chemistry and astronomy, but their eyes are pointed in different directions—astronomy has to do with the ways of great masses of matter in their movements throughout illimitable space, while chemistry reasons about and tries out theories in regard to the ways of particles infinitely small.

The study of chemistry is rather confusing in these days, for two reasons. One is that revelations are coming so fast that it is hard to digest them, and another is that there has been a grand wedding in science within the past few years before the war. Physics and chemistry have been joined together in such intimacy that it is hard to tell where one begins and the other ends. And higher mathematics has entered into the union, so that chemistry to-day has become

## THE HEART OF THE THING

almost as mathematical a science as is astronomy or physics.

Now we shall not enter into problems of mathematics or of physics. I shall not even attempt to tell you how computations are made, for one reason because it would make the book dull reading to those who are not mathematicians, and for another reason because I couldn't if I tried.

Let us, nevertheless, enter into a little discussion as to the nature of matter. In Athenian days it was a popular debate among the Sophists whether, if a particle of matter were divided and one of its pieces divided again, and one of them divided again, and so on and on, granted infinite vision and infinite refinement of work, an indivisible particle would ever be reached. In mathematics one divided by infinity equals zero. In chemistry the name of this ultimate particle on which the Greeks speculated was taken and applied to the smallest particle of any one element that combines. The *atom* has ceased to be the smallest particle imaginable, but it is the smallest unit of substance that we can conceive of any element.

We must get this idea of atoms and molecules and elements clear in our minds, for I shall keep talking about them constantly, and I know very well what will happen to this book if I do not make it clear to you. So let us imagine all matter to constitute a very odd world of mankind. Then the eighty-odd elements would be the different races, some of them very widespread and some of them very rare and hardly known. Now let's call the atoms the individual persons of each race. Then there will be eighty-odd different kinds of atoms, some heavy and some light, some one color and some another, according to the race or ele-

## EVERYMAN'S CHEMISTRY

ment to which they belong. But all the atoms of any one element will have the same qualities.

The individual atoms do not get born and die as we do; they live right on. Do not think about radium or radio-active elements; call that a skeleton in the closet and close the closet door. The individuals or atoms have no sex, but they mate up in pairs or larger numbers, in what we might call families. The families are molecules. There is a great deal of race prejudice both ways, in favor of mating or grouping and against it, among the elements or races. Atoms of two elements that will not combine themselves may be induced to join in a large molecule of many atoms of other elements. Atoms are nearly always found in families or molecules; there are no bachelors or old maids, except in certain metals in a gaseous condition and in the rare gases of the air, like argon, krypton, etc., and let us not think about them. We say sometimes that the family is the unit of society, and it often takes more than a little faith to believe it. When we say that the molecule is the unit of stuff we are nearer the truth. The atoms often wander from one family or molecule to another, sometimes singly and sometimes in groups; and sometimes they do this with explosive violence, while at others they are interminably slow in getting settled. The wandering of atoms from one molecule to another is what we call a chemical reaction.

It is all imaginary, all theory, and yet it is the basis of chemistry. It was said in some verses called "Rollo and His Uncle in Chemistry," at a meeting of chemists, that

You'd better join the church before this course is well begun,  
Because you'll need to exercise the art of faith, my son.

## THE HEART OF THE THING

While we are discussing the nature of matter, we might as well enter a little way into the pleasant fields of speculation about it. For years we have taken it for granted that matter is indestructible. Well, is it indestructible? Is the cosmic universe bounding along, combining elements into molecules of eternal atoms and then dissociating them in a kind of ring-around-o'-rosy without any change except such mere incidents as the drying up of this planet and the birth of another? Are the elements really elemental? Are they primeval stuff? They may be, but they hardly seem so. You will observe later how closely related to one another certain of these elements are, and it would seem that at least those that are closely related have a common origin. And why are some of them always found together?

Then there is radium. It gives off constantly a series of rays with a power beyond any force known to us. Whence comes this energy? And, again, besides these rays it gives forth an emanation which seems distinct from its rays, and which, by itself, decomposes into a radio-active solid and helium gas. Helium is an element. Radium is an element, and yet a part of radium becomes helium. Here is a fact. The theory that matter is indestructible is not so certain, after all.

And this is not all. Combinations of elements are usually more stable than the elements are by themselves. Two parts by volume of hydrogen gas, which they use to fill balloons because of its lightness, and one part by volume of oxygen, a gas which is one-fifth of the air, produce water. In its whole nature water is something entirely different from either of its component parts—less like them than other elements are. It has ways of its own, just as elements

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have. Why, then, just because elements cannot, with the means we have, be divided into other bodies, should we claim immortality for them?

Now let us take another point of view. Imagine, please, a point of space. Not an atom; let's give the atom credit for considerable size. Of course, it's beyond the microscope, but because it's smaller than a wave of light is no reason why we should call it zero. Let's call it large; there's room enough. This point of space that we are imagining is not a speck; it is just a center of force. It is a charge of electricity. Whether it shall have substance or not is according to your pleasure. I think the more usual opinion is that it has no substance, but if it disturbs you to think of it in this connection you might call it primary stuff as long as you think it necessary to do so. That point of space is, let us say, charged positively with electricity. Around and about it whirl other points or centers of force, charged negatively. These are called electrons. They pass the energy along the surface of wires when telegraphic messages are sent. The atom of hydrogen, supposed to be the smallest atom of all, is seventeen hundred times greater than an electron. Doctor Crehore, of Yonkers, who is a great mathematician, has computed the atoms of a number of elements as systems of electrons positively and negatively charged, revolving in their respective orbits very much as solar systems, and providing free energy to give to atoms all their combining qualities. The difference in the organization of these infinitely small solar systems would account for the differences between the elements.

This makes every atom itself a solar system. Whirling units of force, persevering in their orbits so that we cannot break them apart, but definite and

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indestructible only because our vision is so weak, our powers so frail, and our lives so short. They will not always persevere. They will change. Nothing is permanent, nothing immutable, nothing is real throughout the ages.

Strange, how we revert to the philosophy of Bishop Berkeley and the wise sayings of the East, and welcome them as the fashion for our thoughts again—for a season.

But let us get back to the middle of the road, to more concrete things. Please believe that atoms cannot be divided. This is the working hypothesis. We find in practice that the elements cannot be split-up into other bodies. Iron stays iron, gold remains gold, and the same holds true of all of them for all practical purposes. They combine with one another in definite proportions. They not only mix, they combine and produce entirely different bodies. Bring two elements that have a liking for each other together, and just so much of the one will combine with just so much (but not an equal weight) of another.

Here let us consider another interesting postulate called the law of Avogadro. All gases at the same temperature and pressure contain the same number of molecules within the same volume. More concretely stated, there are the same number of molecules in a cubic inch of one gas that there are in a cubic inch of another, provided the temperature and the pressure are the same. Of course, the molecules of one gas differ from those of another in size and weight, but in a gas they are far apart, anyway, and they are supposed to be flying about all the time like so many balloons, hitting one another and bounding back again until they strike something else, and then they bound off in another direction, for they are supposed to be

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very elastic. There is nothing to impede them in their flight through space except either the walls that inclose them or other molecules. It makes no difference whether they are molecules of elements or of combinations; they all behave in the same way. Now I think you will understand what happens when you compress a gas; there is such a bombardment of molecules against the walls of the container that your apparatus will run hot. Keep up the pressure, increase it, and cool your apparatus, and the gas will turn into a liquid. Cooling slows down the motions of the molecules; heating increases it. Then cool the liquid still more and it will freeze or turn to a solid. Some of the freedom of movement which the molecules had in the liquid form is lost; in some way they seem to clinch—and there is the solid. They are not still in the solid, but their movements are much more circumscribed.

In all the chemical world there is no such thing as rest and, except as we may speculate upon it, no such thing as death.

Chemically speaking, then, nature has about eighty kinds or races of matter called elements, and everything there is in nature is made up of them. They enter into combinations with one another and produce bodies that sometimes show a family resemblance, but more often are totally unlike the stuffs that they are made of. They are given to polygamy and polyandry as matters of entire propriety; and if it were not for the fact that we cannot imagine atoms as having sex, the way they shift about in their matings would scandalize any community. They have rules and ways of their own, according to the deductions and findings of wise and observant men, and then again they appear to break them. Therefore chemistry



## THE HEART OF THE THING

is a study accompanied by constant surprises, and the only authority who "knows all about chemistry" is a poor creature, bereft of imagination. There are vast domains in the subject as yet undiscovered, and without doubt some of the favorite hypotheses of to-day will fall by the wayside to-morrow. But you do not have to know all of human nature to become interested in persons, and for the same reason you do not have to read deeply into this subject before its romantic side will begin to appear. If it does not show itself to you, the fault will be mine, for I assure you the romance is there.

You need not try to learn anything by heart. There is an ample index to what is said, and I have no desire to put the burden of memorizing upon you. The task that I have set myself is to keep you interested as you read along, and if I succeed in this I have a feeling that you will want to look things up for yourself, for the chemical view of things is very fascinating, and it takes in all the processes of nature and something of nearly all the industries of man. In fact, I shall confess frankly that I am after something of yours that is not included in the money you pay for this book—I am after your curiosity. If I can get that, there will be no holding you back from the subject.

Please do not be frightened if you see some chemical formulas that appear bewildering farther along in the later pages. I do not think they will worry you, if you will only wait until you come to them. The whole work is designed as a man's book rather than as a torment for the nursery, and so I have not hesitated to enter into some of the profounder problems. But if we only keep good-natured about them there is no reason why they should be dull.

### III

#### PHASES OF MATTER

Solids, Liquids, and Gases—The Ways of Gases—Solutions—Ions and the Ionic Theory—An Electric Battery—Solvents and Solutes—Solid Solutions—Colloids—Difference between Colloidal Particles and Molecules—35,000,000,000 Miles out of a Cubic Inch

WE must, in order to make a reasonable start, go over a few points in regard to the conditions of matter. It is subject to three states—solid, liquid, and gaseous. Water, for instance, is liquid at what we call ordinary temperature, solid ice in the cold, and steam vapor in heat. Most bodies are subject to these three phases at different temperatures and different pressures, although some go over from the solid to the gaseous state almost without entering the liquid phase. They sublime. Iodine is a familiar example.

If we imagine the molecules as each one an individual kind of a balloon, and all of them bobbing around loose, with nothing to hold them together but as though striving to keep as far as possible from one another, they are in the state of a gas. If we imagine them as skipping around every which way over and under one another, sideways, forward, and backward, but held down by a greater tension, we may say that the body which they constitute is in a liquid state. When they clinch we have a solid.

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Even then they continue in motion, dancing around all the time.

We have spoken of the law of Avogadro, whereby it is held that at equal temperature and pressure all gases contain the same number of molecules within the same volume. We note that the molecules are in constant motion and that their bombardment of the walls of the container is what causes gas pressure. Now let us imagine the walls to be absolutely elastic, so that they give way to pressure without opposition. Then for every degree centigrade that any gas is heated, without any increase of pressure from the outside its volume will increase  $1/273$  part, and the container will increase in size just  $1/273$  of its whole. And for every degree centigrade that we cool it, it will contract just that much— $1/273$  of its volume. That is the measure of the drive of a gas against the walls of a container when you heat it. This is why a boiler bursts; its walls are not sufficiently elastic. And if you take an inclosed vessel of air or any other gas at room temperature and pressure and cool it within the container, the pressure will be from the outside in, because the ordinary pressure of the air upon everything is about fifteen pounds to the square inch, while, if you heat it, the pressure will be from the inside toward the outside. The temperature of  $-273^{\circ}$  C. is held to be the absolute zero at which no gas can exist as such; it will be liquid or solid. Do not forget, however, that the molecules are always in motion; more lively in heat than in cold, moving faster and with greater push.

Now let us take a liquid, say water, and put into it some common salt, which straightway disappears. We say it has gone into solution. These particles, the molecules of salt, are there swimming around.

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They spread themselves throughout all the water that is available. If we conduct a current of electricity through the solution, some of the salt molecules will decompose, and, being made up as they are of chlorine and sodium, the one element will hasten to the positive pole and the other to the negative one. Now water alone, pure water, will not conduct electricity, but water containing salt or sulphuric acid or caustic soda or any other electrolyte will conduct it. Those bodies which dissolve in water and whose molecules split up when a current of electricity is passed through are called electrolytes.

Here we may as well consider the ionic hypothesis, which is one of those things that is very possibly not so, or only partially true, and yet it is well to believe it, so as to get at the chemical view of what happens. To quote from the Rollo verses again:

I used to think theology was rather hard on doubt,  
But chemistry, with ions, beats theology all out.

Now please take a fresh grip upon this subject; let's go at it from another angle of vision. We have to do this constantly in chemistry. Some of the molecules of salt, on going into solution and without the need of our conducting a current of electricity through it, dissociated into free chlorine and free sodium atoms in solution, each charged with opposite electrical charges. Let us say they obtained their electrical charges from the force which held them together in the salt. In this state the dissociated parts of molecules are called ions. The freedom of these charged atoms or ions is not so great, after all; there is no such thing as free electricity, so the ions with a positive and those with a negative charge are perfectly balanced. There is an equal number of each sort.

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They are in equilibrium. We have to suppose that these positively and negatively charged atoms or ions behave very differently from the same atoms or parts of molecules when they cease to be ions—that is, when they have given up their electric charges. This statement may not be of thrilling interest at this point, but we must get it recorded.

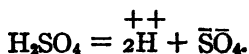
When we put a very little salt into a great deal of water, thus making a very dilute solution, it appears that all of the solute or salt becomes ionized; we have only water and chlorine and sodium ions. As soon as we make it more concentrated, only a part of the salt becomes ionized, and this proportion decreases as the solution becomes more concentrated. It is all theory, pure theory, and yet later on you will see how useful it is. It would not do to say that these ions, these free atoms with electric charges, are the same as ordinary atoms of chlorine and sodium, because if they were we should have caustic soda and free chlorine as the result of putting salt into water. So we say that the ions are so perfectly balanced with positive and negative charges that nothing happens, so far as we can see.

Then suppose you ask why it is, with free atoms of chlorine with a negative charge and of sodium with a positive charge swimming around loose, that they don't combine right up again to chloride of sodium or salt, with all that free energy? I believe the classical answer to such questions is that you are too young, too immature, to understand these things. But the fact is that it has not been answered in any satisfactory way.

Sulphuric acid is another well-known electrolyte, and the formula for sulphuric acid being  $\text{H}_2\text{SO}_4$  (two

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atoms of hydrogen, one of sulphur, and four of oxygen), we find that it dissociates as follows:



But note that these two hydrogen atoms and the  $\text{SO}_4$  group are oppositely charged with electricity. Suppose, then, we put into a jar a solution of dilute sulphuric acid and dip into the jar two electrodes—say, one of zinc and one of graphite, connected with each other by wire. The  $\bar{\text{S}}\bar{\text{O}}_4$  ions will wander over to the zinc, pull its molecules apart, take an atom of zinc for every  $\bar{\text{S}}\bar{\text{O}}_4$  ion, and proceed to shape itself up into molecules of zinc sulphate, or  $\text{ZnSO}_4$ . (Zn is zinc; it has two bonds or units of combining power, so that one atom of zinc takes the place of two of hydrogen.) The two hydrogen ions wander over to the other pole, and, being unable to combine with the graphite for lack of affinity, and the  $\bar{\text{S}}\bar{\text{O}}_4$ , to which they were formerly attached as sulphuric acid,  $\text{H}_2\text{SO}_4$ , being already settled down with the zinc as zinc sulphate,  $\text{ZnSO}_4$ , they do what lone ions always do, if there is an electrode around. As soon as each hydrogen ion touches the graphite electrode it gives up its charge and becomes plain hydrogen again. There is nothing in the solution for it to combine with, and so, being a very light gas, its atoms couple up to molecules and it escapes into the air.

Now we have made sulphate of zinc and produced free hydrogen in our reaction, but we have done something else. As soon as we have connected those two electrodes of zinc and graphite each with a copper wire and connected the wires with a small electric lamp, we find that the lamp glows with light, showing that an electric current is passing through. And the

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current comes from the charge given up by the hydrogen ions where they have touched the graphite electrode, just as its atoms coupled up to molecules and escaped as plain hydrogen gas. On the other side it came from the zinc electrode just as the  $\text{SO}_4$  ions touched it and gave up their opposite charge as they combined with the zinc to produce zinc sulphate,  $\text{ZnSO}_4$ .

Suppose the zinc and graphite electrodes had not been connected with each other by a wire. Then they would not have been electrodes; they would have been just a stick of zinc and a stick of inert carbon dipped into the solution. The sulphuric acid would simply attack the zinc and give up hydrogen at the zinc. The word ion means traveler, and the hydrogen ions would not have traveled over to the graphite and given up their charge over there if there had been no connection of one pole with the other.

I hope the ionic theory will not prove a nuisance to you or discourage you at this point. We need to have an idea of it in our minds because it is the foundation of electrochemistry. Let us reverse the operation and run an electric current through a solution of a salt of a metal. In this instance the dissociated metal ions strike the electrode, give up their electric charge, and, being unable to escape into the air because they are solid at ordinary temperatures, they plaster themselves as molecules right upon the electrode. This is the basis of electroplating, and is the principle of the electrolytic refining of copper and other metals.

We may add a crystalline body to hot water until we have more in solution than will stay there when the water cools. Then the excess will crystallize out in regular, mathematically correct forms, according to its own form of crystals. We can test and measure

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just how soluble any crystalline body is in any liquid at a given temperature and pressure. The liquid is called the solvent, and the body dissolved is called the solute.

So intimately related are solvent and solute that they may almost seem to be a chemical combination; but they are not. A chemical combination is a definite thing—so many atoms of one element with so many atoms of one or more others, and their proportions are fixed. A solution is not fixed in its relations of solute to solvent; the proportions may vary from a trace of the solute to a saturated solution that will not contain any more.

Now suppose instead of taking water we melt a metal and dissolve another metal in it. We can get a complete solution with the same relation of solvent to solute in all the parts. But just as with water, the solvent may not be able to dissolve as much of the solute metal when it cools off as it did when it was molten and hot, and then you can see the excess of the solute oozing out as it cools off. The one will dissolve in the other up to saturation, but no more. When it cools off we have what is known as a solid solution, and here is one of the sportiest fields of modern chemistry.

For instance, when you buy steel you buy it for a certain purpose. You want it to be hard or soft or resilient or to be chemically resistant, or you may want it to give a good cutting edge or to have some other quality. The demand is growing in the steel industry for special products for special purposes. The buyer is growing wise. He is interested in endurance and in the quality of his product in the interest of the Greater Economy whereby his business may keep him for long rather than for a short time. Solutions of



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rare and common metals added to steel even in very small quantities give special and particular qualities.

Again, let us take a substance like gum arabic, that is without form and that will mix with its solvent in any relation, that does not crystallize and that will dissolve and dissolve until a thick paste is reached. Then we have a different situation. Such a non-crystalline body is called a colloid, and its relation to its solvent is not the same as that of a crystalline body.

Many insoluble solids, as, for instance, gold, will enter into colloidal solution if the particles are in a sufficiently fine-divided state. A colloidal solution of gold in water, which requires both art and chemical chicanery to prepare, is a red liquid, and the particles, if sufficiently finely divided, will not precipitate upon the bottom of the vessel.

Colloids have ways of their own that are very remarkable. If a drop of a colloidal solution of gold or a drop of very dilute skim milk is observed under an ultra-microscope, the colloidal particles will be observed to be constantly and forever dancing around. They are never still until a reagent is brought in which clots them. This motion is called the Brownian movement.

I can do no better on this subject than to give some notes that I took at a lecture on colloid chemistry given by Prof. Wilder D. Bancroft, of Cornell University, delivered at a public meeting of the American Chemical Society in September, 1916. It would not be fair to Doctor Bancroft to hold him responsible for the letter of my transcript. I do not know short-hand, and this is mostly what I remember of his talk:

Formerly it was held that a substance was colloidal as distinguished from those that would crystallize. A better definition is that of the colloidal state,

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which has to do with substances divided into very small particles—not molecules or atoms, but still very small. It is the chemistry of grains, drops, bubbles, filaments, and films. It touches every-day life and industry—cement, brick, pottery, varnish, soap, rubber, milk, butter, purification of water, sewage, photography, the great domain of physiology, and then a lot more.

Very fine particles have a greater proportion of surface to mass than larger particles, and every surface can condense other things upon it. For instance, Doctor Cushman found in working on cements that if he got his cement ground to a sufficiently fine powder it ran like water. The reason was the adhesion, or adsorption, as it is called, of a thin film of air around each particle. Every grain had something like a pneumatic tire surrounding it, and so they all ran easily.

If you break a piece of china, the pieces will not stick together well because of the air film on the broken surfaces. Jerome Alexander finds that split pieces of mica will coalesce immediately after being broken, but if left to stand awhile they will not. To adsorb the air film takes time.

It is hard to make two soap bubbles coalesce, because of the air films upon their surfaces. Sir William Thomson found that dried oatmeal takes on water by this same process; that it takes up as much water as sulphuric acid does.

Dyed fabrics are those in which to every fiber of the fabric there adheres a film of the dyestuff.

So-called "acid soils," if washed out with water, will not give an acid reaction to the water; but if wet litmus paper is pressed upon the soil, the paper turns red. This is because the soil adsorbs something alkaline from the litmus paper, leaving some-

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thing acid to predominate and thus turn the paper red. So, whether the soil is properly called acid or not is a problem in the philosophy of Tweedledum and Tweedledee, which he could best explain by the parable of the bananas. Suppose he were to leave a large assortment of both red and yellow bananas on his desk and then leave the room. On his return he finds many more yellow bananas than red ones, whereas before he had to all appearances as many of one kind as of the other. Then the problem to determine is whether some kind friend has secretly presented him with an armful of yellow bananas to add to his store, or the more likely contingency that somebody else has made away with some of the red ones.

The reasons why minute colloidal particles remain in solution are, first, because, being covered by a film of something that keeps them apart, they don't join. Then, looking at a colloidal solution through an ultra-microscope, one sees the particles constantly dancing about in their perpetual quadrille—the Brownian movements, as stated above. But why do they dance? The answer may be found in the comparison of a floating chip with a floating ship. The little ripples cause the chip to be engaged in very lively tossing and pitching, whereas the ship stands still. For the same reason, the colloidal particles, bombarded as they are by the molecules of the solvent, dance about constantly. If the particles are large enough, although the bombardment keeps up, they are not moved by it.

If the protective film which covers the particles be removed by a chemical reagent which dissolves it or precipitates it, then the particles will accumulate in groups, their motion ceases, and they sink or rise according to their weight. They coagulate. On the

## EVERYMAN'S CHEMISTRY

other hand, if all the finely divided particles of a colloidal solution should have a negative electric charge, they will repel one another and remain suspended. The same holds true if all should have a positive charge. Alternating currents of high frequency will often cause them to coalesce and fall down, while direct currents of very high frequency, such as are used in the Cottrell process, drive them upon the baffle-plates set to catch them.

Here end my notes on Doctor Bancroft's lecture.

The line between colloid chemistry and the chemistry of crystalline substances is not at all clear. Indeed, likely as not the distinctions now made are greater than are warranted. We can see by the ultra-microscope the light reflected by colloidal particles. We cannot do this with molecules. By computation, it is said that forty million molecules of a gas, ranged in a row, side by side, would extend the distance of one inch—and I do not even know what gas the mathematical genius who made the computation had in mind. The same authority declared that if the molecules of one cubic inch of gas, at ordinary temperature and pressure, were ranged side by side in a row, the row would be thirty-five billion miles long. I cannot vouch for this; I never counted them. But colloidal particles seem to be aggregates of molecules and yet small enough to be shaken around by the molecular bombardment they receive. We may have to revise our ideas about the size of molecules. Dr. Irving Langmuir, of Schenectady, is beginning to develop some interesting theories in regard to the shape of them. But colloidal particles seem to group themselves together by means of their free energy, with other colloidal particles in indefinite propor-

## PHASES OF MATTER

tions, and thus to provide for an infinite variety of such associations. At least this seems to be the case. It is held by Jerome Alexander, who is an authority on colloid chemistry. But there are those who regard it as unlikely. The study of colloid chemistry, which might be described as the chemistry of uncrystallized matter in very small particles, has shed a great deal of light upon chemical philosophy. There were certain substances which, it was held, would not combine with one another except in solution. Spring, a Belgian physicist, discovered that if they were ground to a fine enough powder and brought together dry under heat and pressure, they would combine. As Professor Bancroft points out, in very fine particles we have a vastly increased surface in proportion to the mass, and that is where chemical energy makes its attack. Another interesting fact lately brought out by Dr. Colin G. Fink is that electrical conductivity will follow the line of smallest particles, other factors being unchanged, and thus show a similarity of action between chemical energy and electrical conductivity. The philosophy of this is, the smaller the particles the closer the contact.

The jingle which follows was written merely to wheedle a little amusement out of colloid chemistry. But as it may indicate something of the Brownian movements of colloidal particles to those who have not had the privilege to examine them through the ultra-microscope, I shall make bold to print it.

### THE BROWNIAN MOVEMENTS

The Brownian movements hold their sway  
And grant no rest the livelong day;  
They also rule the dance all night,  
As you may see by proper light.

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The particles o'er which they rule  
Are like young maids just out of school,  
Or like some youths—the "dancing men"—  
Who work a little now and then,  
But always look at work askance  
When they can enter in a dance.  
And yet these girls and boys are poor,  
Short-winded, listless, slow, and dour  
Compared with particles so fine  
That scorn the music and the wine,  
And whirl and jiggle, up and down,  
And right and left, and almost drown,  
But never stop, and keep it up  
Within the beaker or the cup,  
Or on the microscope's thin slide;  
They chassé every way, and glide  
And shake, and make a ladies' chain,  
And bow and back away again.  
And when you think they're all undone  
You'll find they've only just begun.  
No wonder we grow weary when  
We watch these spots beyond our ken,  
And see them move and whirl and turn  
And twist and wriggle, skip and churn.  
It makes me wild to see them go  
Without a destination; so,  
While watching I'm disposed to shout,  
"Jerome, please turn that arc-light out."  
I've sometimes thought this Brownian whirl  
Was like a boy or like a girl,  
Or rather, if we'd seek the truth,  
We'd find its simile in youth.  
But youth, as I've already said,  
Is too inert, too slow, too dead,  
To be compared with this untiring,  
Everlasting, unperspiring,  
Rocking, jerking, bobbing way  
Of particles by night and day

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That stay distraught, yet permanent,  
In their colloidal tenement.  
And so, I must admit, they strike  
Me as, in fact, being far more like  
A very aged person that  
Has lost his teeth, whose gums are flat  
And smooth, who works his jaw all day  
And chews his senile hours away.  
But similes are all in vain,  
And so we are brought back again  
Where we began: these movements are  
Bewildering and singular.  
The source of most colloidal fright  
Is found in the electrolyte.  
Its advent, though it be disguised,  
Will stop the dance. They're paralyzed,  
The particles. The dance will stop  
And down the particles will drop.  
Well, we're like that. Though young or old,  
We imitate colloidal gold.  
And when the grim electrolyte  
Grips us in his unconquered might  
With skull and cross-bones, then we shout,  
As we fall down: "The light is out."

## IV

### ELEMENTS AND THEIR COMPOUNDS

Faith and the Dream-boy—The Periodic Law—Atomic Weights—Elemental Families—Elements in Life—The Pons Asinorum of Chemistry—Chemical Affinities—Baffling Problems of Valence—Inert Elements—Radicals—Acids and Bases—Difference between Compounds and their Component Parts—A Man in Solution—Catalysis—The Chemical Parson—The Personality of Matter—Carbon's Ways

ON another page at the end of the book you will find a list of the elements as we know them to-day. I think you will find it convenient to consult the list as you go along. I doubt if it is a permanent list. Elements come and go according to the latest findings of one man of research after another. Among the metals, and especially among those found in the rare earths, they are very tricky, and, to tell the truth, it takes more than a little faith to believe in all of them. As elements—that is, as bodies that cannot be resolved into simpler substances by any means at our command—they should be permanent, if not stable, and in practice we shall do well to call them so. Our business is with every-day chemistry, and to regard the whole list as elemental is the best thing that we can do.

And yet the dream-boy will beckon us on. There is the Periodic Law, of which a chemical rhymester once wrote:

The Periodic Law  
Is like a dogma old;  
It is not what we wish it were  
When everything is told.



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Just as imperfectly as *law* rhymes with *were*, so imperfect is the application of this law with the knowledge and means at our command. But let us get an intimation of it into our minds, if we can. It is very interesting. The atomic weight of an element is based on its relative or combining weight. For instance, one volume of oxygen, weighing sixteen ounces, will combine with twice the same volume of hydrogen, which weighs only two ounces, to produce water. Molecules of oxygen and hydrogen contain two atoms each. From this we determine that, counting the atomic weight of hydrogen as one, that of oxygen is sixteen. Now, if we arrange all the elements in horizontal rows of eight, the second to the right of the first, the third after the second, and so on, beginning with the lowest atomic weight and ending with the highest, we shall have a table of the elements, eight wide, like a company of soldiers marching in column of eight. Then, after a little needful rearrangement, we note a remarkable series of relationships, of cousinships we might say, among the elements. It is not those that stand side by side in this table that have similar qualities; the relation between them is as they stand in vertical rows, above and below one another. As we counted them off, in the horizontal rows, they show no special relation to one another. When we consider each as part of a vertical row, on the other hand, we find that the elements of these groups have the same number of hooks or affinities to combine with other bodies; their combinations with oxygen are of a similar nature, and, with frequent exceptions and many differences, they have much in common. We shall note these families as we proceed.

With some, as with potassium and sodium (potash

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and soda), the cousinship is so evident that it may be seen at first glance. You may guess the relationship between gold and silver, but when it comes to the similarities of oxygen to sulphur you may prefer to be told, and even then not believe it with all your heart and all your might. And yet, because of this law, Mendeléeff foretold the discovery of three elements twenty-five years before they were found, and he described what their properties would be and what kinds of compounds they would form. There is a considerable number of other elements that may exist, and, if they do, chemists believe that they know about what their atomic weights will be and something about their properties, because of the vacant spaces in this table of the Periodic Law. There are remarkable recurrent qualities that display themselves in this rhythm of the elements, but these things have been so well described by the late Robert Kennedy Duncan and by Geoffrey Martin in their books that I shall not try to repeat them. There are dreams of the great rhythmic swing of creation in the thought of it; but our business is with the tangible things of to-day and the working hypotheses about them.

In other words, here we have the stuff out of which everything is combined. When I say everything I mean it; the content of every nerve, the place in your brain where your memories are stored and all of the earth as well as all the suns and stars. The brain after death is a different thing from a living brain, but there is no reason to believe that either during life or after death there are more than five or six elements in combination in it at any time.

Without even touching on the mystery of life and its origin, it is interesting to note how few elements make up living things. It is also interesting to ob-

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serve how few elements are here in quantity and how many of them exist only in traces on the earth. The following table, prepared by Dr. F. W. Clarke in 1916, gives the average distribution of the elements in earth, air, and water at the present time. In connection with this table, Dr. Henry Fairfield Osborn calls attention to the fact that life in one form or another has taken up and made use of all the elements of frequent occurrence except aluminium, barium, and strontium, which are extremely rare in life compounds, and of titanium, which thus far has not been found in any living cell. These can be introduced into artificial organic compounds, and it is a fair guess that the Missouri clay-eaters have metabolized some aluminium and use it somewhere in their bodies, all unconsciously. The elements which enter into life forms are *in italics*.

	<i>Earth</i>	<i>Water</i>	<i>Air</i>	<i>Average, including Atmosphere</i>
<i>Oxygen</i> .....	47.17	85.79	20.8 (variable to some extent)	49.85
<i>Silicon</i> .....	28.00	.....	.....	26.03
<i>Aluminium</i> .....	7.84	.....	.....	7.28
<i>Iron</i> .....	4.44	.....	.....	4.12
<i>Calcium</i> .....	3.42	.05	.....	3.18
<i>Magnesium</i> .....	2.27	.14	.....	2.11
<i>Sodium</i> .....	2.43	1.14	.....	2.33
<i>Potassium</i> .....	2.49	.04	.....	2.33
<i>Hydrogen</i> .....	.23	10.67	variable	.97
<i>Titanium</i> .....	.44	.....	.....	.41
<i>Carbon</i> .....	.19	.002	variable	.19
<i>Chlorine</i> .....	.06	2.07	.....	.40
<i>Bromine</i> .....	.....	.008	.....	.....
<i>Phosphorus</i> .....	.11	.....	.....	.10
<i>Sulphur</i> .....	.11	.09	.....	.10
<i>Barium</i> .....	.09	.....	.....	.09
<i>Manganese</i> .....	.08	.....	.....	.08
<i>Strontium</i> .....	.03	.....	.....	.03
<i>Nitrogen</i> .....	.....	.....	78.0 (variable to some extent)	.03
<i>Fluorine</i> .....	.10	.....	.....	.10
<i>All other</i>				
<i>Elements</i> .....	.50	.....	.....	.47

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Where are gold, silver, lead, tin, zinc, and the heavy elements? They are negligible in amount compared to the lighter ones. Look at that absurd silicon; in combination with oxygen it is sand, and as silicates of one sort or another it constitutes part of most rocks. A few tons are reduced (separated from oxygen) daily at Niagara Falls, and this metallic silicon is used in the iron industry to lure the oxygen away from iron and steel; but we haven't found any other general use for it, and we can't eat it. In combination with oxygen all grains use it to form a sheath for their seeds, but its part in life is very slight in comparison with much rarer elements. Again, in combination with oxygen and with different metals we use it as glass; but it is an inert thing at most times and seasons.

This mulling over elements is the *pons asinorum* of chemistry. Along at about this point people are likely to say: "What's the use? Chemistry doesn't tell us anything worth knowing. You might as well say, when I ask you what sort of a fellow John is, that he is made of so many pounds of bone, so many pounds of flesh, and so many square yards of skin. It isn't what I want to know about him at all." Then they drop out and declare that they have looked into chemistry, and that, while it is doubtless a useful study, it is dull and uninteresting.

This would be true if we stopped right here; but we must remember that the study of the elements is only the study of the genealogy of things, and that is not the end of chemistry by any means. Chemistry goes on to study things after they have been produced and to find out what they will do. That is where the romance comes in. It is in combinations of elements that they are interesting, and their com-

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binations are up to more tricks and have more ways of their own than the stuff that they are made of.

Of course you've heard of chemical affinity and the time-worn jokes about it. The subject is not very clear, and, in the light of more precise research, the grand old rules sometimes wobble and sometimes fall down. The list at the end of the book will show you how many hooks or bonds each element has—that is, its valence—and the whole may best be expressed as a display of free energy. Imagine them all to be electrically charged; some at the positive end of the scale and others at the negative end. The farther they are apart the greater their affinity for one another should be, one being very positive and t'other very negative. This rule holds fairly well except that some are much more highly charged than others. Now the number of hooks for combining seem to be separate streams of energy which proceed from each atom, electro-positive or electro-negative, according to its nature, all atoms of each element being alike. This whole subject of valency, which has to do with the number of combining hooks of the elements, is baffling. We do not know nearly so much about the subject to-day as we used to think we did. Usually the rules work, but sometimes they do not. Carbon, for instance, practically always has four bonds, and oxygen two. Then we have carbon monoxide,  $\text{CO}$ , for which there is not any satisfactory explanation. And there are other such compounds. Molecules of elements act very like molecules of compounds, and ions or charged atoms of elements act the same as ions of compounds.

There are great differences in affinity. Sometimes it is so great that bodies combine on contact and in the dark. Others will not combine in the dark, but

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will in the light, for light has a considerable influence on many molecules and seems to start the atoms whirling about in a livelier motion. Many will not combine dry, but will in solution. The most frequent method of bringing molecules into combination is by means of heat. Heat, as we know, is motion among the molecules, and with heat many bodies will combine that will not do so in the cold. Then, again, if we increase the heat enough, we can drive the constituent parts of a body out of combination, some with a little heat, while others cling together so tightly that the heat of the interior of a blast furnace will not drive them apart. And again there is catalysis, which we shall take up later.

Some elements have no affinity at all, and to all appearances will combine with nothing. These are Sir William Ramsay's inert gases of the air—argon, neon, krypton, xenon, and that bewildering helium, that shows up so unexpectedly in the sun, in stars, in certain rocks, and in meteorites as well as in the air. We are not likely to refer to them again. Some elements seem inert, and it appears almost impossible to get them to combine with other elements, owing to the tense, unyielding hold the atoms have upon one another in the molecule. There's nitrogen, for instance, a gas comprising four-fifths of the air. It behaves as though nothing would induce it to combine with anything, and yet, once it is brought into combination, it seems as though nothing would drive it back into single blessedness again. Most explosives are compounds of nitrogen, and when the blow-up takes place the nitrogen is forced out of combination. Thereupon it usually takes up with something else. Nitrogen is the liveliest widower of all the elements, and it will not stay single if there is

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anything else to combine with after it loses its mate. We shall discuss some of its ways when we consider it separately later on.

Now let us again arrange the elements in a row in accordance with their manifestations in the scale of affinity for one another. As we do this, it seems as if some old plutonic parrot of John Silver were constantly crying out the refrain from below, "Pieces of eight! Pieces of eight!" for right here we find the shadow of the Periodic Law before our eyes once more. What is not shadowy at all is their likes and dislikes for one another, which are very strongly marked.

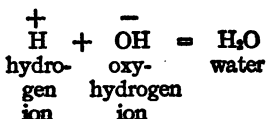
Then we have combinations of elements that act very like the elements themselves—and often more so, to put it in Irish. They are the radicals, or ions of which we have spoken, and are composed of two or more atoms with unsatisfied affinities. Again there are other combinations called acids, on the one hand, and bases or alkalies, on the other; and these range themselves with the elements in the row, the acids with the non-metals, and the bases with the metals. It seems as though there were a distaff and a spindle side to the house—the acids combine with the bases and metals, while the bases combine with the acids and non-metals. The products are called salts. But I think it will only lead us astray to attribute the idea of sex to atoms or to molecules or ions.

What is an acid and what is a base? An acid has a sour taste, and is the opposite of a base—but what does that mean? We have seen how the acids range themselves along the scale of affinity of the elements, on the non-metal side; so the charge is electro-negative. It is not an acid save in the presence of water. This is another statement that is better taken on

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faith than tested out. There always is some water around, in the air and everywhere, so it is just as well not to toy with 100 per cent. sulphuric acid, on the ground that it will be inactive. There is always one or more hydrogen atoms in the molecule of an acid, and these hydrogen atoms are one business end of the molecule, and the rest of it is the other.

I have been urged to elaborate the theory of acids and bases to make the conception of them more clear. Let us put down the acids as electro-negative, and the bases as electro-positive. An acid must have water present, and so must a base. An acid will often attack a metal, but water must be present in the air or on hand to form the metallic hydroxide, the combination with the OH radical. The acid gives up H (hydrogen) ions, and the base gives up -OH ions, and the result is a salt composed of the acid less its hydrogen ions combined with the base less its -OH ions. And besides the salt we have



But some acids and bases are very strong, while others are very weak. Why is this? The same hydrogen will produce weak H ions in one acid, and very powerful or highly charged H ions in another. The same holds true with bases. You may recall that we said the ions were always in equilibrium, that they were balanced, and that for every positively charged one there was a negatively charged mate. Very well, then, if this affinity for one another is very great, the acid or base is strong; if it is slight, it is weak. Let us take sulphuric acid,  $\text{H}_2\text{SO}_4$ , again,



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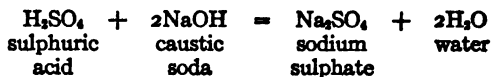
because we are familiar with it. It contains two H ions and one  $\text{SO}_4$  ion. Their affinity is great, and the acid is strong. The hydrogen and  $\text{SO}_4$  ions are separated in the solution, but balanced by a great affinity. Now let us bring that  $\text{SO}_4$  ion within the sphere of influence of the salt of a weak acid, say carbonate of soda, or soda ash,  $\text{Na}_2\text{CO}_3$ . Let us bring the Na ions of the carbonate of soda in between the  $\text{SO}_4$  ions and the H ions with which it is paired in balance. What chance has that poor  $\text{CO}_3$  ion of carbonic acid,  $\text{H}_2\text{CO}_3$ , which is not even known in a free state? It has no chance at all. Right away the sodium ion, Na, is grabbed by the  $\text{SO}_4$  ions, and we have sodium sulphate, or  $\text{Na}_2\text{SO}_4$ . That is a salt. Those two H ions of each sulphuric acid molecule find a weak  $\text{CO}_3$  ion which is being turned adrift. They take up one atom of oxygen to produce water,  $\text{H}_2\text{O}$ , and leave  $\text{CO}_2$  instead of  $\text{CO}_3$ .  $\text{CO}_2$  is carbon dioxide, the so-called carbonic-acid gas which escapes into the air.

There are some acids that need water as much as others do for their reactions, but they do not keep it in their molecules in a free state. Muriatic or hydrochloric acid,  $\text{HCl}$ , is a gas very soluble in water. The true acid should be  $\text{H}_3\text{ClO}$ , because  $\text{HCl} + \text{H}_2\text{O} = \text{H}_3\text{ClO}$ . But only one H atom becomes ionized, not the three. Therefore hydrochloric acid is written just  $\text{HCl}$ , and it is one of the strongest acids known.

A base does business on the metal side. It may be a metal or it may have an oxygen atom with a hydrogen atom attached, an -O-H ion, as it is called. That hyphen on the left of the O (for oxygen) indicates that one of its affinities is free and the other (for oxygen is bi-valent) is engaged with the one hook of the hydrogen atom. Now let us bring an acid and a

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base together and see what happens, taking sulphuric acid and caustic soda.



Do you see what happened? The two hydrogen ions of each molecule of sulphuric acid and the OH ions of the two molecules of the caustic soda combined to make two molecules of water, while the sulphur ion of each acid molecule combined with the sodian ions of both the caustic soda molecules to produce a salt, the sulphate of sodium. So an acid and a base combine to form a salt, with water on the side. A simple test is with the well-known litmus paper, a vegetable dyestuff with which unsized paper is colored. Acid turns it red and an alkali or base turns it blue. All bodies are not either acids, bases, or salts. A great many are, but not all. And you observe that the frequent allusions to acids and bases as male and female are not altogether happy; they do not reproduce their kind; there is no happy progeny of little acids and bases as the result of their combination. They produce salts and water. Chemistry is full of romance, but this is not the place to find it. Some acids are not known in their acid state; they are known as anhydrids—that is, the body which with water produces the acid—and they are also known in their salts. We often speak of carbonic-acid gas, which is carbon dioxide, or  $\text{CO}_2$ . It is not an acid; it is the anhydrid of an acid, and the acid is



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which nobody has been able to produce in an isolated state. But the salts of this acid are among the most widely known. For instance, soda ash, as it is called, is the carbonate  $\text{Na}_2\text{CO}_3$ , of which millions of tons are produced. So the best guess is that it forms, but is too impermanent, water being, let us say, better content to be  $\text{H}_2\text{O}$ , and carbon dioxide to be  $\text{CO}_2$ , than to mate up as real carbonic acid except for a long enough fraction of an instant to conform to the theory—or, to use a biblical expression, “that the prophecy might be fulfilled.”

Chemical compounds have very little in common with the elements which compose them. As I said before, the elements are the genealogical part of the study, and genealogy is interesting enough until you begin to bore people with it, and then we must not blame them if they run away.

I would like to remind you of a few well-known bodies, and point out how vastly they differ from the elements that compose them.

There is sulphuric acid, or oil of vitriol, for instance. It is a combination of sulphur, oxygen, and hydrogen. Nitric acid, composed of the three gaseous elements, nitrogen, oxygen, and hydrogen, is another ruthless agent of destruction. It used to be transported in carboys, which are great glass bottles packed with straw in wooden boxes. As soon as a bottle breaks, up go the straw and the wood in flames. Now, when possible, it is transported mixed with strong sulphuric acid, which may be carried in iron tank-cars for reasons which will be given in the chapter on sulphuric acid.

Dr. Geoffrey Martin tells of a laborer in one of the great German chemical works who fell into a large vat filled with mixed sulphuric and nitric acids.

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Some one heard him utter a shout, but no one saw him. And nobody found him. There was no sign of him to be discovered, or of his hair, his hat, his boots, or his clothes, or his buttons, or the ladle he was supposed to be carrying. He simply was not. The widow wanted her life insurance, but the adjuster developed the theory that he had gone to America. Yet all opportunity for egress from the works was carefully watched, and the records showed that he was still there. His presence in the vat was proved by the percentage of phosphorus which, as a normal man, he was supposed to add to it, and which, without a man in solution, would not be present. That was the proof of loss.

Alkalies are just as insatiate. Caustic soda, caustic potash, caustic lime, combinations of oxygen and hydrogen with the metals sodium, potassium, and calcium are powerful alkalies, and will drive out any frailer bases there may be within reach and combine with their acid partners. Fats are split as with a cleaver with soda, the base combining with the fatty acids to produce soap, and the mild and emollient glycerin is set free. Glycerin is mildly basic in its nature, but it has no chance with caustic soda around.

A very interesting subject in the study of chemistry is called catalysis, and, to my way of thinking, it does more to indicate the whimsical nature of things inanimate, what might be called the personality of matter, than anything else. Let us take two bodies that, according to all the rules and all our reasoning, should combine when we bring them together. They should, but they do not. Of course, there is a reason for this, but what we are after is the reaction. If you strike a match, the reaction will begin from the

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heat of the rubbing. Hold the match to the prepared surface and nothing will happen. Heat makes the atoms move around in the molecule at a livelier pace. They seem to swing in a larger orbit and are more easily caught up by some other matable atom that is swinging around in its molecule. But in these cases nothing happens. We have, let us say, two bodies which should combine, but don't, dissolved in water in one vessel. We heat it and shake it, and still nothing happens. Then we add the catalyst, which is a foreign body, and to all appearances it has no relation to what we have or the combination we want; nevertheless, as soon as it is added, sometimes even in an absurdly slight amount, presto! the solution straightway froths up, there is a grand commotion, and a reaction involving every molecule in the solution takes place. What we wanted to happen does happen. And the little catalyst may be found at the bottom of the beaker just as it was when we put it in, to all appearances, chemical and otherwise, unchanged.

There are volumes and volumes written about this, and there are theories galore, but I shall not develop them. The fact is, the catalyst, which is the active agent in the process of catalysis, behaves generally like a human trouble-maker. The process comes frequently into play in the industries, and by means of it the Germans have been able to carry on the war—as you shall presently see.

Then there is the very opposite, in which such a body can retard or hinder a reaction that otherwise would take place. This is also very like some kill-joys, who, by their mere entrance into a room, paralyze the energy of every one else, suffuse it with silence, and spread inertia. We can find the personal qualities of nearly every one we know in the great

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domain of inanimate things in chemistry. Matter is whimsical!

We have one other subject to consider before we go into detail in this book, and that is the compounds of carbon. Carbon differs from nearly all other elements in that one atom of carbon, with its four hooks or bonds, will use up one or more of them with one or more other elements or radicals and attach all that are left over to another carbon atom. Other elements, except silicon, do not seem to care for this sort of thing, although it does occur, occasionally. Oxygen is sometimes given to the practice, but oxygen has only two bonds, and it is, anyway, much more conservative in this respect. Carbon atoms hook on to other carbon atoms, with hydrogen and oxygen and nitrogen and all sorts of other elements and radicals on the side, but chiefly with the three I have mentioned. Next in order come the halogens, then sulphur and phosphorus.

Carbon compounds, of which there are more than all others put together, are called organic because everything that has life as we understand it (which, for instance, is composed of cells) contains carbon. The name was given long ago when it was thought impossible to produce in the laboratory any of the products of life. The name sticks, and it is not such a bad one, after all. For all the carbon we know has had a history of life at one time or another, and if it takes a stretch of the imagination to refer to asphalt and soap as things having or having had life, it is well that this should be so. We may as well get used to stretching. When we consider the names of wrath that many organic compounds bear, the endurance is submitted to a greater strain.

Carbon has two general schemes of combination.

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First it combines in strings or chains of one carbon atom attached to another, a third attached to the second, a fourth to the third, and so on, as far as you want to go, with all sorts of developments attached to the free affinities on the sides. The other system is known as the aromatic or benzol group of organic compounds, and in these six carbon atoms arrange themselves in a hexagon, or "benzol ring," as it is called, and each carbon atom has at least one affinity free. Then these hexagonal benzol rings mate up with one another and appear as twin rings, as in naphthalene, or triplet rings, as in anthracene, and at each point, where there is a free affinity or where an atom or radical with a lighter grip can be substituted for one with a stronger one, another chain, or another radical, or another element may be added. So the number of combinations is bewildering. We shall consider some of these later on.

## V

### CHEMICAL NAMES AND PHRASES

How They Are Used—Terminations in *ic*, *ous*, *ide*, *ate*, and *ite*—  
The Convenience of Chemical Language—An Attempt to Explain  
Its Ugliness

THE chemical names of substances are indeed words of confusion to the uninitiated. And yet they are useful beyond measure. Of course every substance must have a name, else it could not be catalogued, and we should be unable to distinguish it. It would not do to name them in terms of endearment and romance, like Pullman sleeping-cars—there are not enough names to go round, and that method would be more confusing still. What the chemical name tries to do is to tell what a thing is made of; it tries to describe the molecules, and it succeeds fairly well.

The elements are referred to by their names. I do not want to try your patience, but again I commend to you the table of elements at the back of the book. And yet only a few of them are often met with. Most of them are rare. Compounds of two elements end in *ide*. Thus common salt ( $\text{NaCl}$ ) is chloride of sodium; iodide of potash is  $\text{KI}$ ;  $\text{PbS}$  is sulphide of lead;  $\text{Al}_2\text{S}_3$  is aluminium sulphide, etc. Compounds of one element with oxygen are called oxides, and if there are several different oxides of the same element, the Greek or Latin prefix is used. Thus  $\text{SO}_2$  is sulphur



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dioxide;  $\text{SO}_3$  is sulphur trioxide. With carbon,  $\text{CO}$  is carbon monoxide;  $\text{CO}_2$  is carbon dioxide, etc. Sometimes there is more than one oxide, and the relation of the other element is complex, as, for instance, in the case of iron, of which  $\text{FeO}$  is ferrous oxide, and  $\text{Fe}_2\text{O}_3$  is ferric oxide, because the termination *ic* means more oxygen in the molecule in proportion to the other element than *ous*. The termination *ic* also indicates the engagement of a larger number of bonds of an element than *ous*. The Latin expression for iron is used because you can't make an adjective very well out of iron without the use of *ironic*, which is already pre-empted by literature.

Again,  $\text{FeCl}_2$  is ferrous chloride, while  $\text{FeCl}_3$  is ferric chloride. There are more hooks engaged—the valency is greater in the *ic* compounds than in those ending in *ous*.

With acids, the termination *ic* is the usual one, the one in greatest use or the one first discovered, as sulphuric, hydrochloric, or oxalic acids. If there is a second acid like the first, but containing less oxygen, the term *ous* is used. For instance, the anhydrid of sulphuric acid is  $\text{SO}_3$ , which in effect is sulphuric oxide, although it is usually called "S-O-three," or sulphur trioxide. Add water ( $\text{H}_2\text{O}$ ) to  $\text{SO}_3$ , and we have  $\text{H}_2\text{SO}_4$ , which is sulphuric acid.  $\text{SO}_2$  is the product of sulphur when burned. It is sulphurous oxide because it contains less oxygen than sulphuric oxide. It is also called  $\text{S-O}_2$  and sulphur dioxide. Now add water to it and we have the acid  $\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_3$ , or sulphurous acid. So acids ending in *ous* have less oxygen in the molecule in proportion to other atoms than acids ending in *ic*. But sometimes there are more than two acids. Then the one containing most oxygen has the prefix *per* and the suffix *ic*,

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while the one having the least is *hypo*—*ous*. For instance:

$\text{HClO}_4$ is perchloric acid.	$\text{KClO}_4$ is potassium perchlorate.
$\text{HClO}_3$ is chloric acid.	$\text{KClO}_3$ is potassium chlorate.
$\text{HClO}_2$ is chlorous acid.	$\text{KClO}_2$ is potassium chlorite.
$\text{HClO}$ is hypochlorous acid.	$\text{KClO}$ is potassium hypochlorite.

*Per* indicates beyond, above, and so over, while *hypo* means under or less. Acids with names ending in *ic* make salts ending in *ate*; those ending in *ous* make salts ending in *ite*.

Sesqui means one-half more, so that oxides like alumina,  $\text{Al}_2\text{O}_3$ ; ferric oxide  $\text{Fe}_2\text{O}_3$ , etc., which appear to contain half as much again of oxygen as of the other element, are sometimes referred to as sesquioxides.

The language is not hard to pick up if one only has occasion to use it. It is awkward and unconscionably ugly, but it tells the story better than any other medium that is known. And it is the same in all languages. We shall consider the names in organic chemistry when we get to them.

It is really too bad that the language of chemistry is so ugly. I venture the belief that it is the lack of art in the speech of science that drives people away from considering it. Science has not been much taught except for the last fifty or seventy-five years, and ideas have come faster than good expressions have been found for them, so that science and its language is very like Coal Oil Johnny with his sudden wealth. It has not learned as yet that grace and ease of expression that distinguish the Humanities. Words like "polymerization" and "specificity" are really too awkward for general use, and yet so great has been the need for expression to describe the increasing number of scientific ideas that we have had to be thankful for any old vocal noise that would indicate them.

**PART SECOND**  
**INORGANIC CHEMISTRY**



## VI

### AIR AND WATER

Oxygen—Its Ubiquity and Avariciousness—The Mystery of Sleep—Fire—Ozone—Oxidation and Reduction—Disinfection—Air—Effects of Heat—Freezing-Machines—Doctor Cottrell's Invention and His Use of It—The Unutilized Power of Air Currents—Hydrogen—Water—Why it Rains—What is Man?—He is Twelve Pounds of Ashes and Eight Buckets of Water—Why it is not nearly always winter—Combinations with Water—Hard and Soft Water—How to Soften it—Lime-soda Process—Permutit—Making Water Wholesome.

“THE heathen in his blindness bows down to wood and stone,” but if he had studied chemistry he surely would have worshiped oxygen. We can imagine him engaging in genuflections before an effigy with wings to indicate the air, and the tail of a fish to show forth water, and with as many other attributes as the devout sculptor could affix to it.

Oxygen gives us life—in so far as we cannot live without it for more than a very few minutes. It is the most ubiquitous of the elements. One-half of the crust of the earth is oxygen, so is one-fifth of the air, and so is one-third by volume, but not by weight, of water. We breathe it in in a free state, and exhale, in the place of some of it, carbonic-acid gas, or carbon dioxide, as it is more properly called. You can prove this by buying a little lime-water, pouring it into a glass, and blowing through a pipe-stem or a straw

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into the lime-water. An insoluble, white precipitate is immediately formed which is carbonate of lime. The carbonic-acid gas which you blow out, and which is mildly acid with water, combines with the lime, which is a strong alkali, to form this carbonate. Now marble is carbonate of lime, so that with lime-water enough and wind enough, and the needful procedure in fusing afterward, one might produce his grave-stone out of his own proper person. It would give an aspirant a chance for "a place in the world in the eyes of men" after he had passed away, an opportunity to be both cremated and preserved.

It appears, from researches made in physiological laboratories, that oxygen plays a very important part in what we call the mystery of sleep. Although we continue both asleep and awake to inhale the free oxygen and to exhale oxygen that has done its work of oxidation and is in combination with carbon as carbon dioxide, there is a difference in the comparative *amounts* of oxygen inhaled and exhaled at such times. While we are awake it seems we exhale more oxygen than we inhale. When we sleep we inhale more than we exhale. We deplete the store awake and increase it while we sleep. Now we cannot live without it. It provides by its reactions, by processes of oxidation within us, for bodily heat and for the chemical processes of life. How needful it is we are reminded when we consider how quickly we are drowned.

In the history of torture one of the most cruel methods of putting culprits to death was simply to keep them awake until they died. Without sleep they could not make up for the oxygen lost and so they died of oxygen starvation. It is said that there is no record of the ability of executioners to keep any one

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awake over five days. I make this statement from memory only.

Plants breathe in carbon dioxide and breathe out oxygen. In much less measure, some of them do the opposite.

Oxygen combines with metals to make oxides. Many metals are found in this form. The fires that we see are chiefly carbon and hydrogen combining with oxygen at such a rate that the combining particles grow white hot and give light. Oxygen dissolves slightly in water, and fish get most of what they need that way. It is in rocks and in sand and in all living things. The reason why our bodies are maintained at blood heat is because of the oxygen that is going into combination within them. We are slowly burning so long as we live. If we inhale air that contains much more than one-fifth part oxygen, it makes us hilarious—drunk, in fact. The great melodrama in which the dashing speculator leads oxygen into the air-ducts of the stock-exchange and so excites the traders that stocks go up and he makes his fortune has not been written yet, but here is the chance. I claim no copyright on the idea.

The oxygen atom has two hooks, and there are two atoms in the molecule, except when a current of electricity short-circuits or jumps, as from one cloud to another, and thus produces lightning, and then a little ozone is formed. Ozone is oxygen, but with three atoms in the molecule instead of two, the atoms connected up, as in the corners of a triangle, with one arm or hook engaged on either side. It is not stable; the one extra atom soon disengages itself, and then it is ready for business to oxidize things.

Getting one or more atoms of oxygen into a combination is called oxidation. Getting atoms of oxygen

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out of a molecule is called reduction. Ozone, therefore, is an oxidizing agent. On the other hand, small particles of iron, heated, will take up oxygen from many compounds, and that makes it a reducing agent. A smelter, that melts up ores and separates the free metals from their oxides, is a reduction works. If we imagine the earth as without form and void, we might as well imagine that there was much more oxygen in a free and uncombined state than now, until all the silicon and the metals were oxidized; but that they are now in an approximate state of equilibrium, animals and fires taking it up and plants giving it back to the air again. To produce oxygen for the industries, free from nitrogen, two methods are most frequently used. One is the electrolysis of water, whereby one volume of oxygen collects in a vessel over one pole and two of hydrogen over the other. The other method is by liquefying air and distilling off the nitrogen.

The way to determine whether oxygen is present in excess in a container or a stream of escaping gas is to light a splinter of wood or a straw, blow out the flame while leaving a spark, and then hold the end with the spark so that it will serve as a test. If oxygen is present in excess the spark will burst into flame. A jet of burning oxygen and hydrogen, called the oxy-hydrogen flame, or, better still, oxygen and acetylene gas, known as the oxy-acetylene flame, will make a flame so hot that it is used for cutting iron and steel through almost any thickness.

Oxygen is one of the great disinfectants. If brought into contact with the bacilli of disease it will usually oxidize them and render them harmless. If atmospheric air is pumped into sewage as it comes from city sewers, it will cause all the insoluble organic



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matter to precipitate in the form of stable bodies, at once harmless and approximately inoffensive, and of enormous value as fertilizer. This is the line of research for the economic and harmless disposal of sewage.

The nature of four-fifths of the air we shall have to postpone until we come to nitrogen; but some of the physical properties of air we may consider at this point. It presses in upon us at about the rate of fifteen pounds to the square inch. We live on the oxygen, which is about one-fifth of it. According to its content of water, carbon dioxide, dust, spores of life, a slight divergence in the ratio of oxygen to the whole, and smoke or fumes of one sort or another, it is pleasant or unpleasant, wholesome or unwholesome. The amount of dust that it carries is considerable; indeed, it is the minute particles of dust that diffuse the light and that may have a marked effect upon rainfall. If a beam of light strikes through a dark room, we get an idea of the amount of dust there is floating around. We can see it then. Air is not a carrier of electricity, but the electricity breaks through at times under pressure, as we see in lightning. Moist air is more of a conductor than dry air; that is, electricity breaks through moist air more easily than through dry air. Now pure water is not a conductor, but even the water up in the sky is not absolutely pure. Hardly anything in nature is pure; nature is the most omnivorous mixer there is. Like all other gases, whether chemically pure or mixed, air grows hot as we compress it and cools as it expands.

You may remember some pages back how gases contract as the temperature falls and expand as they are heated— $\frac{1}{273}$  of their volume for each degree centigrade. Now suppose we let a gas expand without

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heating it. While it is expanding it takes up heat instead of giving it off, and that produces cold. When you build a fire under a boiler, where does the heat go? A little of it goes out the chimney, and the rest is taken up by the expanding steam. This explains how they make freezing-machines: by letting liquefied gases evaporate that want to evaporate so badly that they don't need any heat to drive them to it. Then they use up what heat there is. In a similar way, if you compress a gas, not by cooling it, but by force, the molecules will bombard the inclosing walls harder and harder until they grow hot. In time an equilibrium is reached, but during the process it will give off the heat that would have been taken from it had you lowered the temperature.

The inventor who planned to maintain a very high temperature by suddenly compressing hydrogen, which is the lightest gas, and then "keep up the temperature by letting that hot gas escape," forgot to calculate that as much cold would be produced by the expansion of the gas as there would be heat needed for its compression. The reason why it makes your hand cold to blow it is because it causes the moisture to evaporate—to expand as a gas and to produce cold.

Air isn't so light, after all, as we should discover by the way we should puff out and our organs would all be disarranged if we attempted to live in an atmosphere containing all the oxygen we need but with only three pounds' pressure to the square inch—*i.e.*, in an atmosphere within an air-tight room from which all the nitrogen were extracted. Our eyes would pop out and we should burst blood-vessels in no time.

A very interesting and highly useful discovery was made by Dr. F. G. Cottrell while professor of physical

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chemistry at the University of California. He found that under proper conditions an electric current of very high voltage would precipitate particles in suspension in the air. So he studied and worked on it according to his nature, whereby with great eagerness he sought to bring down big game that no other fellow had ever bagged. Then he covered as much of the art as he could with patents.

The results astounded Doctor Cottrell. There were the smelter people, especially the copper producers, in the throes of distress, because in treating the sulphurous copper ores they were either sending forth sulphurous fumes that killed all vegetation for miles around or they were wasting vast fortunes in valuable metal dust that left their stacks and settled down upon the earth like the ashes of an active volcano. The Government was after them, and the farmers were making themselves heard with voices of righteous wrath. So they fell upon Doctor Cottrell's neck, beseeching him to save them. The Cottrell process does not precipitate gases, and so the  $\text{SO}_2$  goes its way. But by this process the particles of metal and earthen dust are removed from the gases *while they are still hot*, whereas by all other efforts to collect the dust from gases it was necessary to cool them first. Now the hot gases, emerging from the stack in that condition, continue to expand until they are cooled off, by which time they are too dilute to do much harm and are very likely to be blown away. The sulphur gas, if cool when it comes from the stack, will sink right down, because it is heavy—and then the trouble begins.

Details had to be worked out, but there was the art established of precipitating particles in suspension and thus saving thousands of dollars daily in single

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plants, and letting the gases escape hot from the chimneys. The royalties bade fair to make a millionaire of Doctor Cottrell in short order—but who wants to be a millionaire? It is, after all, a good deal of a nuisance to be rich. It does not seem to improve the characters of young people to leave them big pots of money. The art of cooking has not developed or improved since the days of Rome, although it is a chemical process; and as for sleeping, a little house is as comfortable as a big one. The administration of a fortune takes up a good deal of time and disturbs one's attention. Of course, we can keep some friends by means of it, but those who need help most are the very men who will need it again—and perhaps be no better for it. Anyway you can put it, it is an infernal nuisance to be rich. Getting the big thing done is the real fun, the real sport, and so Doctor Cottrell organized a good working laboratory in California to treat with the smelter managers and work out their problems in consideration of fat royalties, and then came to New York and organized the Research Corporation, to engage in scientific research. The stock can pay no dividends, and is held by men of consequence for the Smithsonian Institution. He turned over the royalties from all but three Pacific coast States to the Corporation, and used the proceeds coming in to him from the excepted territory to start the thing. Then, when all was in order, he turned over the rights to the excepted States, also to the Research Corporation, and took a job in the Bureau of Mines. It was work that he liked, and the salary gave him a fair living.

The need of this process of electric precipitation of particles in suspension is already very wide-spread. As only one result of its application, enormous savings

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have been made in metallurgy and the nuisance of sulphur fumes greatly decreased. Where the conditions and situation warrant it, the sulphurous gas  $\text{SO}_2$  may be worked over into sulphuric acid, as you may learn later under sulphur, but this is not feasible where the transportation charges for sulphuric acid are too great.

The possibilities of electric precipitation have not been nearly reached yet, and the Research Corporation is working on them. The fumes of iron blast furnaces, for instance, contain, among other things, considerable potash, and by putting high potash feldspar into the charge—another suggestion from Doctor Cottrell's fertile mind—it may result in better iron, more free from sulphur, and the precipitation of a large quantity of the much-needed potash. It is also possible that fog may be dissipated by it, by operating an electrically propelled kite or toy aeroplane, fastened by long wires to the bow of a ship, and between the two poles on the aeroplane and at the bow, precipitating the fog at sea that is in the path of the steamship. At least, this is a possibility.

There are vast potentialities of power in compressed air; a whole undiscovered realm is in this. And with steady winds, such as we have over so much of this country, it does seem as though we were "not very bright" to use so little of it for power, doesn't it? The wind is there, and so is the power; and, with all our great inventive genius, we manage to pump up a little water for the cows! So we had better order some more coal to grind the feed.

Hydrogen is the lightest of the elements; so light that its atomic weight is fixed at one, and the atomic weight of the other elements are multiples of the weight of hydrogen. Refinements of research have

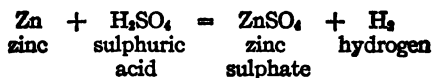
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resulted in fixing 16 as the atomic weight of oxygen, and hydrogen then shows 1.008 instead of 1 in its combinations; but we shall not concern ourselves about this.

Hydrogen has been found in a free state in nature, but only in minute quantities. Most of it that is freed soon combines with oxygen to produce water.

Hydrogen is very widely used in chemical industry. It is easily prepared by the electrolysis of water,  $H_2O$ , which gives two volumes of hydrogen for every one of oxygen. Still another way is to pass steam over finely divided iron or over certain iron ores that are short of all the oxygen that they can carry in combination, heated to a white glow. The steam decomposes to oxygen and hydrogen. The oxygen is taken up by the ore, and the hydrogen passes on through the tubes from which it is collected. Formerly the ore, lean in oxygen, was imported from Germany, but with the ports closed on account of the war, it seemed worth while to look around a little. In Virginia an ore better than the imported was found.

It is also produced by the action of many acids upon metals. Let us consider a reaction we employed once before—zinc and sulphuric acid:



The hydrogen is set free, and, inasmuch as there is nothing for it to combine with, it floats off into the air. After it gets there we know very well what will happen to it.

The ubiquity of water is almost as great as oxygen. In the form of water vapor it is mixed with air. In Samuel S. Sadtler's interesting book *Chemistry of*

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*Familiar Things* he gives the number of grains of water that one cubic yard of air will contain as the maximum of humidity at various temperatures by the Fahrenheit scale. Here they are:

14 degrees.	26.8 grains.	68 degrees.	206.5 grains.
32 " "	58.6 " "	86 " "	362.1 " "
50 " "	112.6 " "	212 " "	1 lb. and 81 " "

He adds that one cubic mile of air, saturated with moisture at 95 degrees Fahrenheit, would give up 140,000 tons of water (say 35,000,000 gallons) if cooled to 32 degrees, or the freezing-point.

No wonder it rains! The rays of the sun, which produce no heat by their passage through space, do produce heat by their passage through the air, and at the surface of the earth, where the greatest density prevails, the greatest heat is produced. So they vaporize the waters of the sea and lakes and rivers until the air becomes more or less saturated, according to its temperature. A breeze of cold air up in the blue, that we may not feel at all, reduces the temperature of that above us and down comes the rain.

Water is the great natural solvent and carrier. A man has been described as about twelve pounds of ashes and eight buckets of water. A watermelon is ninety-six to ninety-eight per cent. water.

A peculiar and very important trick of water is that just as it freezes it expands about 6 per cent. in volume and decreases in weight or density in proportion. That is why ice floats. If it did not float, rivers and streams would freeze solid and—things would be different in the spring!

Hydrogen peroxide,  $\begin{pmatrix} \text{H} - \text{O} \\ | \\ \text{H} - \text{O} \end{pmatrix}$ , or  $\text{H}_2\text{O}_2$ , is a rather

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unstable fluid, usually dispensed in dilute solutions in water, from which the extra oxygen atom soon frees itself under the reaction  $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$ . It is the well-known oxidizing agent of the household medicine-chest, and it really is an excellent antiseptic for that reason. We put it on a sore finger to oxidize the foulness, to burn it up without appreciable heat.

Water has remarkable properties. It behaves very like an element in many respects. It makes innumerable chemical combinations with other bodies. Many bodies will dissolve in water and crystallize out as hydrates which are compounds with water. For instance, washing-soda, which is sodium carbonate,  $\text{Na}_2\text{CO}_3$ , is a white, amorphous powder by itself, but it will combine with water and go hot in the process until the decahydrate, which means the tenfold hydrate of sodium carbonate, is formed and this is expressed as  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ —that is, ten molecules of water to one of soda. These crystals are known in every kitchen. Copper sulphate by itself is a white substance which crystallizes in colorless needle-like prisms. It will combine with water, five to one, to make the pentahydrate, or fivefold hydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) which crystallizes in big blue crystals of an entirely different shape and popularly known as blue vitriol. Heat will drive the water off.

We often speak of hard and soft water, and, while we know the difference in practice, we are not all of us acquainted with the philosophy of it. There are two metals, calcium and magnesium, that are related to each other in the periodic system, and they have certain qualities in common. Calcium oxide,  $\text{CaO}$ , is lime, and magnesium oxide,  $\text{MgO}$ , is magnesia, and neither is very soluble in water. Both build salts with carbonic acid. By contact with the rocks



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the water with carbon dioxide,  $\text{CO}_2$ , in solution, takes up some of these metals and carries them in solution as bicarbonates. Now, roughly speaking, the bicarbonates are soluble, while the carbonates are not; so if you boil the water you shift the bicarbonates over into carbonates—and down comes boiler scale: your carbonates of lime and magnesium, plus mud held in the water in suspension. This is what is called temporary hardness—the bicarbonates of these two metals in solution that precipitate or fall down as insoluble carbonates when the water is boiled. But there is what is known as permanent hardness, when the water contains the chlorides and sulphuric acid salts of these metals. Boiling will not bring them down. And yet, in proportion as the water contains salts of calcium or magnesium, it is called hard. The German scale is universally used as to the hardness of water; one degree of hardness represents one part of lime in 100,000 parts of water, two degrees is double that, etc. Water of no more than three degrees of hardness is generally held to be pretty soft. But we do not want any lime or magnesia in water for many industrial purposes, whether in a soluble form or not. In washing, bleaching, scouring, dyeing—in nearly all textile works—soap is used. In laundries and households we use it, too. But what is soap? It is, as a good example, stearate of soda (stearic acid is a fatty acid). It is soluble in water. But if the water contains calcium or magnesium there are immediately produced calcium and magnesium soaps, which are insoluble. The stearic acid shifts over to all the Ca and Mg that is in the water, and we have useless lime or magnesium soap, which makes a gray ring on the bath-tub, streaks the clothes in the laundry, confuses the dyer, and costs all sorts of money in wool-

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scouring and in the bleaching industries by sheer waste of soap. West of England woollens have a good reputation primarily because the water there is soft—about three degrees of hardness being the average. Calcium and magnesium are not wanted in water used in the industries.

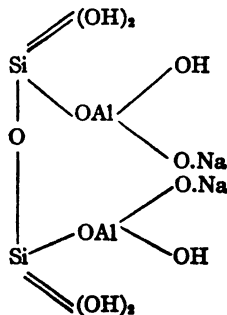
We need not enter into a discussion of the nuisance that hard water is in boilers; the scale ruins the tubes, and it is such a poor conductor of heat that it runs the coal consumption away up. There are all sorts of compounds sold to prevent boiler scale, and they are usually, if they have any merit at all, designed to act chemically on the water and produce a scale that is lighter and more porous and so more easily removed. Such compounds are soda ash, tannin, caustic soda, and also some acids. Others act mechanically on the particles of scale as they form, and surround them with a slippery film to keep the mass from hardening or cementing together. Such compounds are slippery elm, starch, fats, and oils. And many of them are out and out quack medicines. Honey, soap, mercury, tobacco, urine, and cow-dung have been sold as wonderful *practical* remedies.

The lime-soda process was the first scientific method introduced to make hard water soft. It consists of a great tank for settling, and smaller tanks for reagents, with a view to bringing down the soluble salts of Ca and Mg as insoluble precipitates. The process requires the attention of a chemist, and it does not completely soften the water. This method will bring water down to four or five degrees German hardness—four or five parts lime or magnesia in 100,000 parts of water, but not lower.

Now comes a modern invention called "permutit" that is chemically interesting and is of great useful-

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ness. Dr. Robert Gans, of the German Geological Survey, while studying the fertility of soils, found that certain substances known as zeolites have a remarkable quality of swapping bases *whenever they find a chance to do it*. They take up potash, then exchange it for something else as the plants are ready for the potash, then exchange that something else for more potash, and they keep it up indefinitely, feeding potash to the plants in this manner. Of course, the zeolites of the soil are too weak, too mixed with other things, to be commercially valuable, so he proceeded to make artificial zeolite by fusing feldspar, kaolin, pearlash, and soda together. It is a double silicate of aluminium and soda with water. Graphically it is said to be represented by the following formula:



I pray you not to let it frighten you. You observe those two Na or sodium atoms on what we might call the eastern boundary? That is where the peculiarity lies. If you bring a solution containing magnesium or calcium into contact with it, it will exchange sodium for Mg or Ca, and then, if you bring another salt around, it will exchange its Mg or Ca for the base contained in the new solution. It has, in other words,

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no principles of loyalty, no faithfulness, no morals whatever. We are accustomed to polygamy in chemistry; it does not shock us, but this "power of exchange" is unique.

Now let us apply this quality to our own use. An upright cylinder contains a layer of marble chips over a perforated bottom in its upper part. Below this is an air space, and then comes a thick layer of permutit, which is a substance very like soapstone in appearance, being very porous. This also rests on a perforated bottom, and under it is a layer of gravel. The water, in passing through this filter, exchanges every particle of its lime and magnesia for sodium, in whatever form these may be. It makes the shift, and at the end of the day (according to its computed capacity) you have a lime and magnesium permutit in the filter instead of a sodium permutit, as in the morning. The water that has passed through it is completely soft; it is of zero hardness. In the place of all its Ca and Mg it contains soluble Na salts. Soap is not wasted in it, boiler scale does not form, and the water problem, in many cases, so far as hardness is concerned, is settled. But the filter is to be used next day, and the permutit, being combined with Ca and Mg, has nothing to exchange for these elements. So we flush out the filter by forcing water through it backward for a few minutes and then make a 10-per-cent. solution of ordinary cooking salt (chloride of sodium, NaCl) in water. This we let stand in the filter during the night, and by morning the water in it has become exceedingly hard and the permutit has become sodium permutit and is ready for business again to soften water. The permutit is *not* soluble in water; it will only exchange bases with salts in solution. So it is not wasted, it does not get

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tired as some catalysts do, and it lasts permanently, day in and day out, making its perpetual exchange. The amount of salt required to regenerate the permutit is about one pound of salt for every one hundred gallons of hard water softened. It is a very pretty operation, and as useful in the household to produce the luxury of soft water as it is in the industries.

Iron and manganese are also troublesome factors in water. Both make stains on cloth. These are removed by oxidation, the higher oxides of these metals being insoluble. There is a modification of permutit which also removes them.

Manganese especially is not desired in city water-supplies. So far as we know, its presence does not seem to affect the health of persons who drink water which contains it, even when we consider mineral waters that are high in manganese content. But it is a nuisance—worse than iron. Certain microscopic growths found in water-pipes absorb the manganese into their sheaths and form long, fibrous, gelatinous masses which increase the friction of the water, and when they are loosened by heavy currents the water issues from the faucets in an unsightly condition. It is deadly to fish life. The brownish cast of the water shuts out the sunlight and stunts the fish growth, and the oxide of manganese accumulates in and clogs up the fish-gills. Like iron, in laundries it produces brownish streaks that show on ironing, and in bleacheries it produces a muddy-white color and occasionally brownish spots. It will do the same to the finer classes of white paper if employed in paper-mills. It injures the fermentation processes of breweries, and it spoils the color baths of dye-houses.

A great contribution to the health of cities and villages has been found in the addition of a slight

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amount of chlorine to the water-supply. Since the adoption of the chlorination system by the New York City department of water-supply, not a single case of typhoid fever has been attributed to city water.

Another method of destroying bacteria in water is by submitting it to the action of ultra-violet rays. These are rays that are substantially light rays—or rather would produce light if our eyes were equipped to observe them. They are the burning, actinic rays of the sun—the freckle rays and sunburn rays. The method is to use a mercury arc-light which produces many ultra-violet rays, but which cannot get through glass. They do, however, go right through quartz. So the Peter Cooper Hewitt mercury arc light is produced in a quartz tube and then water is run over the tube.

## VII

### MORE ABOUT AIR

Nitrogen—Its Inertia—Nature's Subtle Art—The Need of Fixed Nitrogen—Its Satanic Tricks—The Lean Man and the Fat One—The History of an American Invention—How the Great War was Made Possible—A New Method of Fixing Nitrogen that is Full of Promise—Ammonia—Nitric Acid—Why Explosives Explode

**N**ITROGEN, N, is a gas, a little lighter than oxygen—in the ratio of 14 to 16—and it comprises about four-fifths of the air. There is enough going on in the air to keep it pretty well mixed. We have already spoken of how inert this nitrogen gas is. We breathe in the air, take up the oxygen (of which nearly all of the other fifth is composed), and breathe out the same nitrogen, but not the same oxygen. In the exhalations the nitrogen is mixed with some oxygen and carbon dioxide, or carbonic-acid gas, instead of all of the oxygen that went in. Nothing happens to the nitrogen. Its atoms are clinched together in pairs as molecules, and they will not loosen up under ordinary conditions. In a temperature such as is traditionally held by orthodoxy to be reserved for sinners, we should have an entirely different chemistry of every-day life; for extreme heat, such as is found in the electric spark, will tear the nitrogen molecule apart, and when nitrogen once begins to react, the cosmic fur may be said to fly.

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Nature in its quiet way performs the most difficult laboratory tricks without any noise or explosion. I have said that it is very hard to get nitrogen from the air into combination. I meant in the laboratory or in the works. On the other hand, clover, cow-peas, and other leguminous plants have little nodules on their stems just above the earth, and these nodules swarm with harmless bacteria which take the nitrogen from the air, bring it into combination, and feed it to the plant. Plow under your cow-peas or clover and you will have provided your soil with fixed nitrogen. This is the good old standard way to get fixed or combined nitrogen into the soil. The only objections to it are the need to hurry up, the demand for farm produce from increasing urban populations, the desire of the farmer to exchange produce for wealth, and the sleepless mortgage.

Aside from taking up nitrogen from the air, nature has a way of giving it back. There are a few chemical reactions that give off free nitrogen out of combination, but it is quite a laboratory trick to perform them. Nature, on the other hand, seems to give it off in some sort of a cycle, taking it up by means of bacteria, and giving some of it off again when the plants and animals are carbonized; and there may be—who knows?—some bacteria that consume nitrates and set nitrogen free. There must be a nitrogen cycle, into life and back again.

But there we are. We must have nitrogen in combination for fertilizer and so for food, for clothing, for explosives, for mining, and for all sorts of engineering work and for munitions of war, for dye-stuffs, and hundreds of other things. Some foods, such as sugar, starch, and fats, contain no nitrogen, but the proteins, the stuff that builds muscle and



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brawn, the meat for strong men, all these contain nitrogen.

Of course, there is the great waste of city sewage, which contains enormous quantities of nitrogen in combination, and we know how to turn it all into in-offensive and useful products. I say we know how, but we have not, all of us, these facts of chemistry alive in our brains, and so we just go on complaining and wondering why somebody doesn't do something.

Let us now consider a little more of this remarkable element. It can outdo fire and brimstone in its satanic tricks. It will not combine except in its own secret way, and once it gets into combination it becomes the business end of nearly all explosives, and it is one of the elements which must be present in combination if life is to prevail. In the eggs of all animals it is present in large proportion. I shall not offer to base any conclusions upon this, but merely give it as a fact, that the thin, wiry little man, who is all nerves and action, contains more nitrogen in proportion to his weight than the obese, fat man. It is present in all nerve stuff.

Until lately the only place to get nitrogen in combination was from the great nitrate-of-soda beds of Chile. Ammonia is obtained from the distillation of coal, but not in sufficient quantities. This source of supply is increasing as by-product coke-ovens are built. That comes from the N left over in the plants during the ages. We can get it into the earth by planting leguminous plants and plowing them under, as we have noted, but for manufacturing purposes the Chilean nitrate beds were practically the only source of supply. This is what has made Chile so rich.

But that store will not last forever. The best posted persons say that at the present rate of consumption

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it should take from a hundred to a hundred and fifty years to exhaust the supply, and for the past twenty-five or thirty years the problem of "fixing nitrogen," as it is called, has been one of the chemical prizes. As soon as nitrogen is in combination it is fixed, and the chemist feels that he can negotiate with it.

An American, Charles S. Bradley, was the first to combine nitrogen and oxygen from the air on a factory scale by means of an electric arc at Niagara Falls. He made considerable progress, developed the art, in fact, but he had the misfortune to be first in the field. American capital has never been favorably disposed toward experiment except in mechanics, and at the point that Bradley had to stop for lack of funds two Norwegian chemists, Birkeland and Eyde, took up the problem. With the greater water-power available in Norway, and with abundant capital from Europe, they have had enormous success. Before the Panama Canal was opened their ships with nitrogen fertilizer sailed from Norway around Cape Horn and past Chile to the west coast of the United States with their product. They make a combination of nitrogen with lime for fertilizer.

Then the Germans took hold of it, and we shall see what happened. The results are not due to any special superiority of German chemists over others. The merit of a chemist depends upon the man, not his nationality. We may hold this fact to be self-evident, but there are a great many of us who do not seem to have grasped it yet. Of course there are more chemists in Germany than there are elsewhere in proportion to the population, and I think it true that the profession has a better social standing there than in other countries. This may sound like tea-parties and dances, but it means directorates and banking connec-

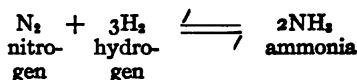
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tions. The main feature, however, is that German business men are not afraid of that bugaboo of his American cousin, to-wit, "the theorist." American capitalists will take up an engineering problem and look over blue-prints and plotted curves which they do not completely understand, but which they will try to grasp, and as soon as they get the idea of what is to be accomplished and a theory of the method, down comes the telephone receiver, and a syndicate is formed. The money is straightway available. If the problem is a chemical one, it has been his habit to close his mind and his eye and to have nothing to do with it, whereas his counterpart in Germany would go at the proposal with the same lively curiosity and interest that he would display in response to a proposal in engineering. The result is that the American business man has neither experience in, nor knowledge of, chemistry. He cannot tell one chemist from another. He doesn't even know where to go to find out. Not long ago some Eastern capitalists took under consideration a large investment in a chemical works engaged in the utmost niceties of chemical manufacture. The processes were involved and exceedingly complex. So, in order to get at the bottom facts concerning the industry and the way the problems were met, they sent a civil engineer out to examine it. They might as well have sent a dentist!

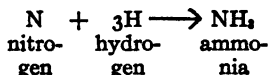
Now let us get at the way the Herren Doctoren Haber and le Rossignol solved their part of the problem. There is very little water-power in Germany, but catalysis is an art, and it is available everywhere. They knew, as every chemist has known for years, that if three volumes of hydrogen gas and one volume of nitrogen are inclosed in a vessel and an electric spark is passed through the mixed gases, a little

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ammonia will be formed. Ammonia is three hydrogen atoms hooked on to one nitrogen atom. Its symbol is  $\text{NH}_3$ . Not much ammonia will be formed, though, and for this reason: at the temperature of the electric spark, nitrogen and hydrogen will unite to form ammonia, but, at the same time, ammonia is not stable at that temperature. It will decompose into nitrogen and hydrogen. It is reversible reaction, because it works both ways. It is expressed as follows:



But they did not want a reversible reaction; they wanted the straight reaction, one in which the arrow points in one direction only, and not both ways.



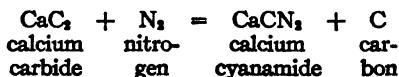
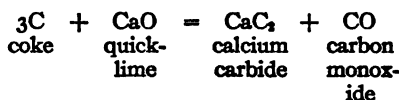
So they conceived the happy idea of sending one part of nitrogen and three parts of hydrogen through tubes containing various metals with a view to getting the metals to act as catalysts. Osmium and uranium did it. Details of the process are secret, but by 1913 an enormous plant, costing \$10,000,000, had been erected and was in full operation at Ludwigshafen. The nitrogen is obtained by making liquid air and distilling it off while the hydrogen is obtainable in many ways. This gave Germany all the combined nitrogen it might care to produce by adding the units already established, in the form, you observe, of ammonia.

It never rains but it pours. When one process is developed, another is likely to follow shortly after-

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ward. An American chemist, Willson, started to make calcium carbide years ago at Niagara Falls by treating coke and quicklime in an electric current. It takes considerable power to bring this about, but only one-fifth as much as is required to fix atmospheric nitrogen by the Norwegian process. Calcium carbide is a very widely known chemical to-day, and is used to make acetylene gas for lighting houses, for automobile lights, and for enriching city gas. The reaction is very simple; put water on it, and the product is acetylene gas and slacked lime.

Now we shall strike a very good example of the international nature of science, of how an invention is started in one country and developed in another. Here we have calcium carbide, developed in the United States. Then two German chemists, Frank and Caro, discovered that if you heat this carbide and run a current of nitrogen over it, the nitrogen will combine with it and you have calcium cyanamide, which is an excellent nitrogen fertilizer. Let's put these two reactions down:

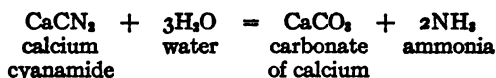


The extra carbon is burned away in the heat, and the cyanamide fertilizer was made in large quantities in Germany.

Now we come to a third reaction that has been known for a long time—that superheated steam passed

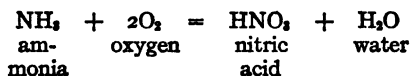
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over calcium cyanamide gives as the resultant products carbonate of lime, or limestone, and ammonia. Here is the reaction:



So here were two methods of making ammonia, and from the way in which the output of calcium cyanamide has increased in Germany, from 50,000 tons annually before the war to 600,000 tons in 1916, it would appear that the cyanamide process is the cheaper one.

In the mean time the great Professor Ostwald had worked out a method of turning the base ammonia into nitric acid, also by catalysis. Nitric acid is one nitrogen, one hydrogen, and three oxygen atoms in the molecule, and Professor Ostwald found that by passing ammonia and oxygen through tubes filled with finely divided platinum the following reaction takes place:



Nitric acid is the one thing most especially needed to make explosives. By 1915 Germany within her own borders had developed the art of making all things needful for munitions of war except copper and cotton. Without these processes the war could not have lasted over a year, despite the enormous stores of Chilean nitrate that were on hand. Indeed, it was these four processes of Willson, of Haber and le Rossignol, of Frank and Caro, and of Ostwald that have made the

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war endure. Courage would have been of no avail without them.

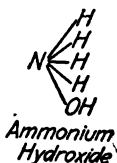
Very lately Prof. John E. Bucher, of Providence, Rhode Island, has proposed a new method. His work is based on the fact that nitrogen will combine with an alkali and carbon in the presence of iron as a catalyst and produce the cyanide, a combination, for instance, of sodium, carbon, and nitrogen,  $\text{NaCN}$ . He brings soda ash and powdered coal together with powdered iron or iron ore—either will do—in a furnace, runs air through it at a moderately high temperature, and the result is sodium cyanide, with the iron uncombined. No electric power is needed, no heavy outlay, no costly materials; the whole process, apparently, may be carried out almost anywhere at a very low cost.

Of course everybody knows that cyanide of soda is not a thing to fool with; that it is a deadly poison. But by treating it with steam the products become sodium bicarbonate and ammonia. Engineering details still need to be worked out, and nothing can be called a success until it succeeds in practice; but it is not more than fair to say that Doctor Bucher is busy at them. If the difficulties are overcome, it bids fair to make us all sit up and take notice.

Now let us study the combinations of this absurd element with hydrogen and see what results we get. I do not know why nitrogen behaves so. There is ammonia,  $\text{NH}_3$ . It has an avidity for water which is almost insatiate. But when you have  $\text{NH}_3$  dissolved in water ( $\text{H}_2\text{O}$ ) you haven't exactly what you might think you have. As soon as the ammonia reaches water, or as soon as you start a chemical reaction going, the nitrogen in the ammonia molecule brings its two extra hooks or bonds into play, the

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molecule of ammonia combines with a molecule of water, and we have ammonium hydroxide, or  $\text{NH}_4\text{OH}$ . Let us put it down graphically:



Here you get a radical or tail of oxygen and hydrogen just like the OH radical in caustic soda or caustic potash, and *it behaves that way!* It acts just like a metal, but like a metal with one bond. Drive it out of such a combination, and we shall find that the nitrogen has only three hooks again. And then, having determined that ammonia behaves like the metals, we should expect it to have no special affinity for them. But here we should be wrong again, for it attacks metals with energy, just as an acid does, giving up its hydrogen and forming nitrides of metals. That *ide* in nitride, you may recall, indicates direct combinations of a metal with nitrogen. Nitrogen makes other compounds with hydrogen, foolish compounds which it has no business to make, such as hydrazine,  $\text{N}_2\text{H}_4$ , and hydrazoic acid,  $\text{N}_2\text{H}$ , all bristling with unsatisfied bonds. Hydrazoic acid is unstable, and very explosive as well.

With oxygen it forms  $\text{N}_2\text{O}$ , or nitrous oxide, which is laughing-gas, and is largely used as an anesthetic. There is nitric oxide,  $\text{NO}$ , which is unstable, and combines immediately with more oxygen to form nitrogen dioxide,  $\text{NO}_2$ , which is a reddish gas and violently poisonous. Then we come to nitric acid anhydrid,  $\text{N}_2\text{O}_5$ , which, with one molecule of water ( $\text{H}_2\text{O}$ ), makes



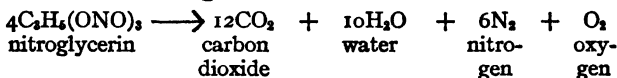
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two molecules of nitric acid ( $\text{HNO}_3$ ), one of the most powerful acids known:



"Acids," says the definition, "have one or more hydrogen atoms that can be replaced by metals." All right; there's nitric acid, but there's ammonia,  $\text{NH}_3$ , too, which is not an acid. Then there's the opposite: "Bases, or alkalies, include compounds of the general type of metal having an OH radical." Very well; there is ammonium hydroxide,  $\text{NH}_4\text{OH}$ . But why does nitrogen work both ways? From the standpoint of a lazy, old-fashioned chemist, I should say that nitrogen has no chemical conscience whatever.

Since nitric acid has so much to do with explosives, we might as well consider a little about them at this point. An explosive is a substance that is capable of liberating large quantities of gas as a result of very rapid chemical action. The gases set free by the explosion of gunpowder occupy about three hundred times the volume of the powder, and the heat of the explosion expands these gases many times more. In gunpowder the carbon and oxygen atoms that unite to form carbonic-acid gas and other bodies are in different molecules, and the explosion, while instantaneous in appearance, is not so rapid as dynamite. In nitroglycerin all the atoms are in the same molecule, which disintegrates as follows:



These gases take up twelve thousand times the volume of nitroglycerin in the dynamite, and by the heat produced are expanded nearly eight times farther. So one cubic inch of it expands about nine thousand times in an instant. No wonder it shakes things up.

## VIII

### THE RED-HEADED HALOGENS

Fluorine, Chlorine, Bromine, and Iodine—Four of a Kind, with Differences—The Young Devil and the Old Man with a Past—Muriatic Acid—Salt—Great Value of Chlorine—Purification of Water—Uses of Fluorine, Bromine, and Iodine

HERE is a family of elements, legitimately connected according to the Periodic Law, that behave just as a family of persons or elements should behave. We are wont to attribute to men and women having auburn hair a certain quickness in response to a stimulus. This is a distinct quality of the halogens. As the persons we have in mind grow older we observe that they usually grow more sedate and circumspect. As the halogens increase in atomic weight they grow more biddable and quiet in their reactions. Young persons adorned with Titian locks, if they be maids or young matrons, are likely to wear green gowns. We shall find this taste in color also indicated among the halogens.

They are fluorine, chlorine, bromine, and iodine. Their atomic weights are, in the order named, 19, 35½, 80, and 127. In the same order they are gas, a gas twice as heavy, a liquid, and a solid. In color they are, also in the same order, greenish yellow, yellowish green, brown, and violet-black. All of them have one hook or affinity. All of them combine with

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hydrogen and produce acids, and, in the order of their atomic weights, their liking for hydrogen decreases. Bring fluorine and hydrogen together, even in the dark, and they will combine to HF, or hydrofluoric acid, with explosive violence. The real acid would be hydrogen fluoride, HF, with water,  $H_2O$ ; but as there is always water around and only one hydrogen atom becomes ionized, we call HF hydrofluoric acid, HCl hydrochloric acid, etc. Chlorine and hydrogen will unite under the influence of light. Bromine will unite with hydrogen if passed through a heated tube containing platinum gauze. It takes still more heat in the presence of platinum black to do the same with iodine. Then, again, fluorine will drive chlorine out of combination with hydrogen and take its place. Chlorine will do the same to bromine, and bromine to iodine. Compounds of iodine with hydrogen are not very stable, but you can hardly drive fluorine and hydrogen apart—until HF meets something that fluorine likes better, as, for instance, an alkali, a metal, or a salt with a weak acid. Then the hydrogen is dropped, and the fluorine goes at it. We might say that fluorine is the young devil, and iodine is the old man with a past. In valency, too, bromine and iodine grow a little irregular. Occasionally they develop three, five, and even seven bonds for combining. This does not appear to be the case with fluorine, and chlorine seems to be slightly addicted to allotropy, but we do not know much about that yet.

The family relations toward oxygen are the very opposite. Fluorine does not combine with it. Chlorine does, but the compounds are very unstable. Chlorate of potash, for instance, gives off its oxygen with explosive violence in the presence of a reducing agent. O. compounds of bromine are more stable than those

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of chlorine, and those of iodine are more stable still. With sulphur they behave in a somewhat similar manner.

All the halogens are lively in their reactions, fluorine being the liveliest, and iodine the least so.

Fluorine, because it bites its way through glass and destroys tissues with such avidity that it is one of the rankest of poisons, is no laboratory favorite. Of all the elements it has the strongest tendency to form compounds. It is found in nature mostly in rocks, in combination with calcium as fluorspar. Its principal use is for etching glass. The process is interesting. The glass vessel which is to be etched is covered with wax, which is not disturbed by the fluorine or by hydrofluoric acid. The desired figures are drawn in the wax, leaving the glass bare wherever the lines are. Sulphuric acid will drive fluorine out of fluorspar, producing sulphate of calcium, or gypsum, on the one hand, and hydrofluoric acid on the other. The glass is attacked wherever a line is drawn, or wherever the wax is scraped off. An opaque surface is produced. If the hydrofluoric acid is dissolved in water, and the glass, prepared in the same way, is dipped into the solution, the acid will bite out a shiny and transparent groove wherever the glass is exposed. Ammonium fluoride ( $\text{NH}_4\text{F}$ ) is generally employed in the place of fluorspar in the glass industry. Another use for this product is to eat the silicates out of straw and then limber it up so that it may be woven into straw hats.

Chlorine is the famous member of the family. It is of very widespread occurrence. In combination with sodium, one atom of each in the molecule as chloride of sodium ( $\text{NaCl}$ ), it is what we know as salt, common salt, table salt, and we must have it.

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When it is scarce we prize it, and when it is lacking we will brave almost any danger to get it. I do not know what its function is in the process of digestion, but it is probable that the hydrochloric acid which we have in our stomachs is prepared from salt in one of that series of co-ordinated chemical factories that each of us has in his body. Chlorine is everywhere in varying quantities—in rocks, in the earth, in the sea, and deposited in the beds, far under the earth, of extinct salt lakes. Nature does not perform a cycle with salt; it washes it into the sea and lets it stay there. The actual process seems to be that the sodium is carried to the sea mostly in the form of the sulphate, and the calcium or lime as a chloride, and a shift in the acids takes place after a while in the seawater, the calcium chloride becoming calcium sulphate or gypsum, and the sodium sulphate becoming sodium chloride. The sea is growing richer and the earth is growing poorer in salt. But we need not worry about it.

Salt is the raw material for the great soda industry, which we shall treat of in another chapter. It is also used to drive other bodies out of solution in chemical industry.

Like all other members of the family, chlorine combines with hydrogen as hydrochloric acid or, as it is often called, muriatic acid, one atom of each in the molecule, or  $\text{HCl}$ . It is, as we have mentioned before, not really an acid until water is brought to it, so that the proper formula would be

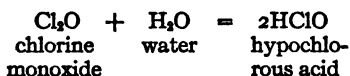


But we write it  $\text{HCl}$  because the water stays water and the one  $\text{H}$  ion of  $\text{HCl}$  does the business.  $\text{HCl}$  is

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a gas, very soluble in water, and is a very strong acid. It is very widely used to produce metallic chlorides. Many metals are dissolved by it. It has wide-spread use in the industries. The grape sugar works take large quantities to neutralize the lime in the process. Some steel-makers use it for "pickling," or eating off the oxides, or rust, from manufactured steel, although sulphuric acid is more frequently employed for this purpose.

Chlorine combines with oxygen, always to form acids. The natural combination is one atom of oxygen to two of chlorine (because of the oxygen's two hooks and the chlorine's one), or chlorine monoxide,  $\text{Cl}_2\text{O}$ . This is a brownish gas, very dangerous and very explosive, breaking up easily into its component parts. Mix it with water and you get a solution of hypochlorous acid, in which a molecule of water will combine with a molecule of the chlorine monoxide to form two molecules of hypochlorous acid. This may explain it:



It cannot be separated, but its salts are known, and they are great bleaching agents. The reason why is because it gives off oxygen so easily. Thus potassium hypochlorite,  $\text{KClO}$ , becomes potassium chloride,  $\text{KCl}$ , plus oxygen. The Cl slips around the O to get at its favorite, K, which it likes better than O. There are a number of other combinations of chlorine with oxygen, all of them acids, and there is always the likelihood of the oxygen atoms wandering away to any other mate that they can find. A neat little experiment to show this is to mix some powdered sugar and some chlorate

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of potash together, carefully, and then add a drop or two of concentrated sulphuric acid. The whole mass will immediately burst into flame, because the sulphuric acid will drive the chlorine dioxide from the chlorate of potash, and chlorine dioxide will not endure for a minute if there is anything as easy to oxidize as sugar at hand. Sugar is composed of carbon, hydrogen, and a little oxygen.

One of the chief uses of all of these halogen compounds with oxygen is as oxidizing agents. Oxygen does not seem to feel comfortable when combined directly with a halogen.

The greatest use of chlorine in a free state or loosely combined is as a bleaching agent. The way it works, theoretically, is that one molecule (or two atoms) of chlorine gas and one molecule of water unite to form two molecules of hydrochloric acid ( $\text{HCl}$ ) and set free one atom of oxygen. But chlorine, as well as hydrochloric acid, eats into and disintegrates fiber, so that laundries which use this easy bleaching agent have become the bane of the man with shirts and the distress of the housewife with her weekly wash. Washing clothes is a chemical problem, by no means made perfect as yet, although progress has been and is being continually made. What bids fair to be an even greater use is in the disinfection of drinking-water. Very small quantities of it will effectively destroy bacterial life by oxidation, as we have explained, even in the effluent from sewage.

Now that the electrolytic method of producing soda has made chlorine plentiful, and since it is easily liquefied (by cooling and compressing) and shipped in convenient cylinders, there is no more excuse for the spread of epidemics through drinking-water. A little apparatus in the gate-house of a large municipal

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water-supply will effectively chlorinate every bit that is used. The effluents from sewage-disposal plants, if treated with chlorine, may be safely allowed to flow into rivers without fear of contaminating the water.

In his work on *Municipal Chemistry*, Professor Baskerville brought out, several years ago, the value that minute quantities of chlorine would have if added to the water with which streets are flushed. It was later urged by Albert H. Hooker in his book on *Chloride of Lime and Sanitation*. Here we have the greatest disinfectant known to man, at once cheap and available. And we have in the dust of our streets the bacilli of tuberculosis, tetanus, and the germs that are said to be active in spreading coughs and colds, besides a lot more of the kind. But so far as I know the sprinkling of streets of a city with chlorinated water has never been thoroughly tried out yet.

Bromine is used in medicines, the many bromides having the effect of inducing sleep. Compounds of bromine also are availed of in the dyestuff industry.

Iodine is principally used in medicine and also in laboratories as a reagent in analysis. There is a very large quantity of it contained in seaweed, and the new potash industry of the Pacific coast, whereby potash is extracted from giant seaweed or kelp, will probably be glad to hear of a good process whereby iodine may be extracted economically as a by-product.



## IX

### SULPHUR, SULPHURIC ACID, AND SULPHUR COMPOUNDS

Sulphur's Cousinship with Oxygen—*Dr. Jekyll and Mr. Hyde*—Herman Frasch's Clever Device—A Few Sulphur Combinations—Sulphur Oxides—Sulphuric Acid—The Old Horse of Chemistry—Its Uses and How it is Made—Chamber and Contact Processes—The Chemical Bank—Thiosulphates—Note on the Element Selenium

**S**ULPHUR is related to oxygen under the Periodic Law, although it does not look like it or smell like it or make combinations that resemble those of oxygen in appearance; it is only when we consider them chemically that we note the cousinship. We shall touch upon these resemblances as we pass them by.

Sulphur, like certain other elements that we shall consider later, displays what are rather awkwardly called "allotropic modifications." We have spoken of the personal quality of matter, especially within the domain of catalysis, and here we have another manifestation that indicates how like persons matter is. Many books besides *Dr. Jekyll and Mr. Hyde* have been written about the phenomenon of dual or multiple personality in individuals. Now allotropy is this multiple personality in elements. We recall how oxygen is a gas of the air, and that the same oxygen may become ozone. The same holds true of sulphur. It may be crystalline, and as such it crystallizes into

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two forms. It occurs in an amorphous state as a powder, and as a liquid it has two forms—that of a mobile liquid and that of a viscid one. All the time it is sulphur, chemically pure sulphur, and nothing else. We know how to bring these changes in form about, and there is probably some regrouping of the atoms in the molecules which causes the changes.

Sulphur, like oxygen, has two hooks or affinities to combine with other atoms; but, unlike oxygen, if it needs more than two it displays four, and in still other combinations it avails itself of six. I do not know of any relation between the number of hooks an element shows for combining and its allotropic modifications.

Sulphur is found in volcanoes and in direct combinations with metals which are called sulphides. In Louisiana and Texas there are enormous deposits of this element in a free state deep under the quicksand, and most of the supply for the United States comes from this source. It is obtained by the process devised by the late Herman Frasch, who sank through the sand a six-inch, a three-inch, and a one-inch pipe, one inside of the other, and through the six-inch pipe he forced water, superheated and under pressure of one hundred pounds per square inch. Through the three-inch pipe he drove hot, compressed air, and this, mingling with the sulphur which the superheated water had melted, caused it to flow up through the one-inch pipe. A screen at the bottom of the one-inch pipe keeps the earth out, and very pure sulphur comes up, is cast in tanks, and housed in great blocks. In Europe the chief source of supply is Mount Etna, in Sicily, and it is also found in extinct volcanoes in Japan.

When we consider that sulphur combines with other

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elements very much as oxygen does, we can see what a vast number of sulphur compounds are possible. And it can produce more different kinds of evil-smelling combinations than any other element.

Just as oxygen and hydrogen combine to produce water,  $H_2O$ , so sulphur and hydrogen combine to produce hydrogen sulphide,  $H_2S$ , which is a gas and smells like rotten eggs.

Sulphur unites with the halogens somewhat after the manner of oxygen, but with entirely different results. There is, for instance, the chloride,  $S_2Cl_2$ , which is a liquid with a nasty odor and has the capacity to dissolve sulphur. The bichloride,  $SCl_2$ , is also known, as well as is the tetrachloride,  $SCl_4$ , and there are other halogen compounds.

With the metals it unites directly to form sulphides, just as oxygen forms oxides. Some of these sulphides of metals are the crystalline iron pyrites, copper pyrites, cinnabar (mercury sulphide), galenite or galena (lead sulphide), zinc-blende (zinc sulphide), which are well known, but there are very many more of them. In combination with iron, as the amorphous sulphide of iron, it is a powder without any mechanical qualities. Sulphur makes iron brittle when present even in very small quantities. Coal that contains too much sulphur ruins boilers and grate-bars; in fact, sulphur is a great nuisance in fuel.

With carbon it combines to produce carbon bisulphide,  $CS_2$ , which will dissolve sulphur and rubber and which in the impure commercial state smells like destruction. One whiff of it is enough to fix it in memory. It is used as an insecticide, and in chemical industry to produce carbon tetrachloride, in the production of artificial silk and for other purposes.

It is with oxygen, however, that sulphur forms the

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compounds which bring it into most frequent commercial use. There are four of them known:

Sulphur sesquioxide	$S_2O_3$
Sulphur dioxide	$SO_2$
Sulphur trioxide	$SO_3$
Sulphur heptoxide	$S_2O_7$

Of these we shall consider only two, the dioxide and the trioxide, and this brings us to the consideration of what we may call the Old Horse of Chemistry, or sulphuric acid.

When you get up in the morning and turn on the water for your bath, you use a nickel-plated faucet which required sulphuric acid in its manufacture. Your tub, if it be enameled, has met sulphuric acid before it became what it is; and if it is an old-fashioned one of tin, plated on sheet copper, it needed even more sulphuric acid before it took its place in civilization as a bath-tub. The water in which you bathe has probably been treated with sulphate of copper to clear it of algæ. The towel with which you dry yourself has met sulphuric acid before you bought it, and the soap-maker possibly found it necessary to use some in the preparation of your soap. The bristles of your hair-brush have been treated with it, and the back of your brush, as well as your comb, if they be of celluloid, could not be produced without it. Your razor, before it reached its present high estate, may have been pickled in sulphuric acid after it was annealed.

As you put on your underwear you may recall that the bleacher and the dyer used sulphuric acid on the thread before it was knit or woven, or upon the fabric afterward. As you button up your outer garments you may be reminded also that sulphuric acid was

## SULPHUR

needed in scouring the wool, in making the dye, and in the process of dyeing the cloth.

The button-maker needed some before your buttons were complete. The tanner needed some in making the leather for your shoes, and it is also used to produce shoe-polish. The cushion upon which you may rest your pious knees in your devotions has met sulphuric acid in one way or another more than once before it reached its present dignity.

At breakfast your cup and saucer may have come into being without the aid of sulphuric acid, but only provided they are plain white. To produce the constituents of *aqua regia*, which dissolved the gold for gilt ornamentation, sulphuric acid was used. The silver of which your spoon, knife, and fork are made may come from a smelter which has first burned the sulphurous ore and made sulphuric acid of the fumes, while if they are silver-plated, they were plated in a sulphuric-acid bath. The farmer who raised the wheat of which your rolls are made probably used acid phosphate on his land to encourage the wheat to grow. Acid phosphate is phosphate rock treated with sulphuric acid. The paper-maker needed some sulphonated aniline blue to tint your morning paper, even if he used no sulphite pulp, and it would be a rare ink that is innocent of the touch of sulphuric acid at some point in its history.

If you eat buckwheat-cakes and syrup, the syrup needed it, and as for your artificial light, if you get up early enough to need it, you would be driven back to candles if it were not for this product. It is needed in the refining of kerosene and gasoline, and as for your electric light, brought to you by currents of electricity through copper wires—where would the electric-light industry be with-

## EVERYMAN'S CHEMISTRY

out copper? And where would the copper industry be without the electrolytic process of refining, which requires enormous quantities of sulphuric acid? It would be paralyzed.

We have heard of the embarrassment of industry by the lack of German dyes, but that is a mere bagatelle compared with the general break-up that would follow a dearth of sulphuric acid. We can neither go to war and have smokeless powder nor can we live in peace without it. Wherever you go in civilization you cannot get out of its path. You may never see it, you may not know its qualities and its very remarkable chemical personality, and you had better not touch it, but almost invariably it has been around before you.

All of this will explain but a fraction of the all-pervasive ubiquity of sulphuric acid in the arts of what we call civilization. And its use is growing along with the development of chemical industry and the science of agriculture.

It has been known as a commercial product in the United States since 1793. The first step in the process of making it is to burn sulphur. When you burn sulphur you produce a gas containing one atom of sulphur to two of oxygen in the molecule. Everybody knows the choking smell of this gas; you used to produce it every time you lighted an old-fashioned sulphur match. It is easy enough to produce it on a small scale, but when it comes to doing this very thing on a large scale, and measuring the units by the ton, it will be seen that even here there are engineering problems involved that are far from easy. And we haven't sulphuric acid yet, by long odds. We have with our two atoms of oxygen to one of sulphur the anhydrid of sulphurous acid, the first

## SULPHURIC ACID

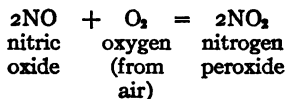
step in the process: what we are after is the anhydrid of sulphuric acid; we must worry another atom of oxygen into that molecule and make  $\text{SO}_3$  instead of  $\text{SO}_2$ . If we leave it by itself an indefinite time and allow plenty of air to weaken it, it will change over as we want it to, but we never could make a commercial product that way. No, we must introduce an oxygen-carrier into the chamber that contains the gaseous product of our first step—something that will not only give up an atom of oxygen, but find a taker in each molecule of  $\text{SO}_2$ . Oxides of nitrogen will do this, and then get back the oxygen they have lost from the air, so that they may be used over again and again with very slight loss. That is the way we get our  $\text{SO}_3$  in the old chamber process which we shall now describe.

As the first step, either sulphur is burned or the sulphurous ore is roasted and the fumes of  $\text{SO}_2$  are passed first through a dust-flue and then through what is called a Glover tower, the purpose of which is to get a thorough mixture of the gases wanted. This is a tower filled with lumps of inert material, and there trickles down through the tower sulphuric acid containing oxides of nitrogen which are dissolved in it. The sulphurous fumes ascend against this stream, carry along the oxides of nitrogen, and proceed into great leaden chambers. Steam is blown into the chambers at various points. Here a complicated reaction takes place, but in effect nitric oxide,  $\text{NO}$ , unites with the oxygen of the air to form nitrogen peroxide,  $\text{NO}_2$ . Then—



## EVERYMAN'S CHEMISTRY

and then, again—



and the cycle is complete. So we have sulphuric acid on the floor of the chambers, and the gaseous oxides of nitrogen, which must not be lost, mixed with air. From the last chamber the gases are led into a tall Gay-Lussac tower, filled with coke, and over which, from the top downward, there trickles concentrated (78 per cent.) sulphuric acid. This dissolves the oxides of nitrogen, but not the air, which passes out through the stack. The concentrated acid with the oxides of nitrogen dissolved in it is then pumped over from the bottom of the Gay-Lussac tower to the top of the Glover tower, where it proceeds to give up the oxides that it has in solution, just as described above, and this process goes on over and over again. The sulphuric acid taken from the chambers is of about 65 per cent. strength, and this is usually concentrated by boiling off the water in pans made of a very high silicon iron.

There is no such trouble in getting water attached to the  $\text{SO}_3$  molecule as we had in getting that extra atom of oxygen into it. The trouble is to keep the water away. The acid that comes out of the leaden chambers is strong enough for use in some industries (for instance, to produce acid phosphate for fertilizers), but it is not strong enough for general commercial purposes. Not all the water is boiled off in the concentrating-pans; you cannot produce a 100 per cent.  $\text{H}_2\text{SO}_4$  by this concentrating process, but it is made strong enough for a great many purposes—for most purposes, in fact.



## SULPHURIC ACID

Dilute sulphuric acid must not be shipped in iron containers because it will eat right through the iron, whereas strong sulphuric acid may be shipped in tank-cars if the necessary precautions are taken to keep water out. This, according to a plausible theory, is because the salts of iron, produced by the action of the acid upon the iron walls that contain it, are very soluble in water, but insoluble in strong sulphuric acid, and thus make a protective coating to the inside of the walls which cease to be protective as soon as the solvent water is introduced.

The contact process is an achievement in catalysis and is a development of the last twelve or fifteen years, so far as practice is concerned. It consists in inducing the sulphurous fumes ( $\text{SO}_2$ ) to unite with oxygen of the air and form  $\text{SO}_3$  in the presence of one or more catalysts. The pyrites are roasted, and the cinder, consisting chiefly of iron oxides, but also some oxides of copper, arsenic, and other metals, are used as the first step in which about one-half of the  $\text{SO}_2$  (mixed with air) is converted to  $\text{SO}_3$ . This is a black, dirty gas, mixed  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$ . From this point it is cooled and cleaned and scrubbed according to the process employed and the conditions at hand, until a gas of remarkable freedom from foreign matter is obtained. This is especially necessary because the remaining half of the  $\text{SO}_2$  is still to be converted to  $\text{SO}_3$ , and the slightest amount of arsenic or any of a number of foreign substances or dust will "poison" the catalyst so that it will not do its work. So far is this purification carried that among the greatest producers the gas will stand the Tyndall test; that is, that a beam of very concentrated light passed through a dark chamber containing it will not show a particle of dust. When we think of the myriads of

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dust particles we see if a beam of ordinary daylight is let into any living-room that is darkened, we can imagine how well this work of purification has been done. The gases are then passed over devices containing platinized asbestos, and by the time this process is completed practically all the  $\text{SO}_2$  is converted to  $\text{SO}_3$ . From this point the process is very like the old one; the  $\text{SO}_3$  is caught up by strong sulphuric acid, which not only absorbs  $\text{SO}_3$  until it becomes 100 per cent.  $\text{H}_2\text{SO}_4$ , but 100 per cent. sulphuric acid will also dissolve the anhydrid.

Let us get this a little clearer.  $\text{SO}_3$ , you recall, is the anhydrid which with water,  $\text{H}_2\text{O}$ , produces the acid  $\text{H}_2\text{SO}_4$ . If you have an acid that is 90 per cent. sulphuric acid and 10 per cent. water, then, as  $\text{SO}_3$  is added to it, the acid will gradually become 100 per cent. sulphuric acid. As soon as this stage is passed and we have what is known as free anhydrid dissolved in the sulphuric acid, it is called oleum. This is likely to have about 20 per cent. free anhydrid. If the anhydrid only is wanted—*i.e.*, the fuming, solid  $\text{SO}_3$ , without any  $\text{H}_2\text{SO}_4$  in it—the  $\text{SO}_3$  is usually distilled off from the oleum by gentle heating.

Some claim that the contact process will in time supplant the chamber process, and I think it likely, in the course of a pretty long time. The reason is that, under ideal conditions and flawless management, it should cost no more to make, say, 97 per cent. sulphuric acid by the contact process than 65 per cent. chamber acid. But it takes years to achieve a very high degree of administrative efficiency, and the process is more delicate, and there are patents covering all sorts of steps in it, and royalties must be paid—and the chamber process is easy. I think the chamber process will still be in operation when many

## SULPHURIC ACID

of the young fellows of to-day will be referred to as graybeards.

Lately the United States Department of Agriculture has proposed still another method that is similar to the old one, except that instead of great leaden chambers for the reaction, it is proposed to use coils of lead pipe. The laboratory tests are promising, but no large-scale tests have been made, and the proportion of surface to volume is so different in laboratory tests from that in practice that a great deal must be done before it is known what value, if any, the proposed method has.

This heavy, oily fluid, also known as oil of vitriol, that destroys nearly everything with which it comes in contact, is like fire or water or electricity—a good servant but a bad master. And yet it is about the safest and most biddable chemical we know, considering its strength. And in its strength is its greatest usefulness. We do not employ a Percheron stallion to draw a baby-carriage, and yet the Percheron stallion is just what we do want for a heavy load on a bad road. Now sulphuric acid is one of the great dray-horses of chemistry. But if we carry the equine simile any further we shall get into difficulties, for the main business of sulphuric acid is to bite into things chemically and play hobs generally, under control. All of its get, its progeny, its colts, or, more properly speaking, the sulphates and sulpho-conjugations, are not soluble in water, but so many of them are that it is fair to say that one of the principal lines of business of this chemical is to make things over so that they will dissolve in water. Phosphate rock is thus made more available in practice for the soil. Being an acid, it will neutralize alkali, and a new use for great quantities of acid produced from smelter fumes in the

## EVERYMAN'S CHEMISTRY

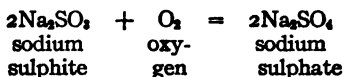
West has lately been proposed in the reclamation of alkali deserts.

The founders of the Chemical National Bank of New York many years ago started in business making sulphuric acid. In those days it was made according to a "formula" or recipe: burn so much sulphur, and do thus and so according to rule and gather in your product. There were difficulties of transportation and in manufacture because sometimes the chambers would become sick and not perform their allotted tasks, while the demand for the product was irregular and slight. So the proprietors closed out their business, and, having a charter bounded hardly short of their imagination, they started a bank. Now the career of that bank has been so honorable, so useful, and so distinguished for sound business methods that we are bound to rejoice that the Chemical Bank was duly started. But those interested in chemical industry cannot wholly free themselves from the wish that the same talent for organization and the same high character which qualified those men for banking might have remained to help along the chemical industry in this country in the days of its struggles. We might have been further ahead than we are now.

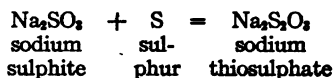
I have intimated that sulphuric acid is the old horse of chemistry. Then soda would be the old mare. And there is lime. Lime, let us say, is the mule, which carries off great loads of waste.

Before we give up the subject we must consider a little trick that sulphur has in working its way into molecules, very like the way of oxygen in oxidation. For instance, a sulphurous acid salt, if left in the air long enough, will go over, by oxidation, into a sulphuric acid salt:

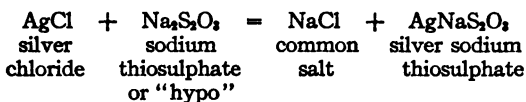
## SULPHUR COMPOUNDS



Now, if we digest sodium sulphite with finely divided sulphur for some time, the sulphur will work its way into the molecule in the same way, and we have:



There are other ways of doing this, but we shall not discuss them. The point is, we have what the name implies, a sulpho-sulphate, because the prefix *thio* is taken from the Greek word *θειον* (*theion*), which means sulphur. Thiosulphuric acid is not known in a free state, but we have its salts. The sodium thiosulphate is called by photographers *hypo-sulphite of soda*, or "hypo," and is used to dissolve the chloride or bromide of silver from those places on the photographic plate where it is not wanted. We shall see how useful it is when we consider photography. It forms a soluble silver sodium thiosulphate as follows:



The element selenium is very like sulphur in its reactions. It is also, like sulphur, known in various forms or modifications. It is a brick-red powder, a black, brittle, glassy mass, a red crystalline form, and a gray metal. It is sometimes found in the deposits of Glover towers and chambers of sulphuric acid

## EVERYMAN'S CHEMISTRY

works, and it has been found in meteoric iron. Its chief claim to fame is that in the metallic form it conducts electricity very much better in the light than it will in the dark. This has led to numerous inventions and some curious apparatus, among others the "electric dog" of J. H. Hammond, Jr., of Gloucester, Massachusetts. A little four-wheeled wagon is equipped with a chemical battery, and selenium resistance coils are placed back of glass lights which are supposed to represent eyes. If a strong light is thrown upon them, this turns the selenium resistance coils into a conductor, and the "dog" speeds forward and follows the light, being propelled by a storage battery which it contains. The light causes the selenium coils to conduct the current from the battery to the motor.

The commercial supply of selenium is obtained from the electrolytic copper refineries. The present American production is about thirty thousand pounds per annum. Elementary selenium is most largely used to give a red color to glass (for railroad signal-lights, etc.), and it is also employed to overcome the green color of glass. Selenite of soda is used to impart a bright red color to enamels. Selenium is also used to a limited extent in medicine and bacteriology.

## X

### PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

Phases of Each—Relations to Nitrogen—Phosphorus Fertilizers—Matches—A Real Triumph in Manufacturing—The Ironmaster's Torment, and Why He Swears—Fish-bones for Brain Food—The Unaggressive but Poisonous Arsenic—Its Uses—Antimony and Its Trick of Expanding—Use in Type-metal and in Alloys—Bismuth

**P**HOSPHORUS belongs to the same group as nitrogen. It is not found in a free state in nature because of its marked affinity for oxygen. It has, like nitrogen, sometimes three hooks and sometimes five, according to its pleasure. When driven out of combination it is a heavy, crystalline solid, yellowish in color, and it melts at  $44^{\circ}$  and boils at  $290^{\circ}$  centigrade. In this form it is a rank poison. But if we heat it in a closed vessel it turns into a reddish brown powder which is stable and inert and has little poisonous action, because of the difficulty of absorption. There is an intermediate scarlet phosphorus, and yet another violet or black modification, all chemically pure phosphorus, but constituting allotropic modifications, such as we observed in sulphur, and showing different phases of the same substance.

Phosphorus combines with hydrogen to produce phosphine,  $\text{PH}_3$ , just as nitrogen produces ammonia,  $\text{NH}_3$ . Phosphine is a very poisonous gas and has a disagreeable odor, something like spoiled fish. Just

## EVERYMAN'S CHEMISTRY

as ammonia,  $\text{NH}_3$ , dissolved in water,  $\text{H}_2\text{O}$ , produces ammonium hydroxide,  $\text{NH}_4\text{OH}$ , which is known only by its salts, so we get with phosphine,  $\text{PH}_3$ , in water,  $\text{H}_2\text{O}$ , phosphonium,  $\text{PH}_4\text{OH}$ , which is also known only in its salts; that is, no one has ever succeeded in producing by itself either ammonium,  $\text{NH}_4\text{OH}$ , or phosphonium,  $\text{PH}_4\text{OH}$ , although there are plenty of salts in which an acid radical takes the place of the OH. Phosphonium is not so strongly alkaline as ammonium.

Then there is a metaphosphoric acid,  $\text{HPO}_3$ , just like nitric acid,  $\text{HNO}_3$ , but an entirely different product, and by no means so strong an acid. A more important compound with oxygen is known as phosphorus pentoxide,  $\text{P}_2\text{O}_5$ , which is a white, voluminous, snow-like mass, which takes up water to produce orthophosphoric, or, as it is generally called, phosphoric acid,  $\text{H}_3\text{PO}_4$ . This pentoxide is the most powerful dryer known. It will absorb water, if present in sufficient quantity, down to one milligram of water in forty thousand liters of air.

About one-tenth of 1 per cent. of good soil is phosphate, and plants need it. So do animals. As plants exhaust it from the soil it needs to be replaced, and from this requirement comes the great phosphate fertilizer industry. The effect of phosphates upon plant growth seems to be to increase the prolificacy and to hasten the maturity of the crops. The exact rôle that it plays is still rather vague, but its effect is seen in increased crops. There are in the United States vast deposits of minerals, chiefly in the form of various phosphates of calcium. They are found in South Carolina, in Florida, in Kentucky, Wyoming, and elsewhere. This country is very rich in phosphate rock and exports vast quantities of it to Europe in



## PHOSPHORUS

normal times. To prepare it for fertilizer the rock is ground fine and treated with about an equal weight of sulphuric acid. The product is called "acid phosphate" in the fertilizer industry and is applied to renew the phosphorus taken from the soil by plants. We have had the curious situation in this country of the manufacturers of acid phosphate urging the farmer to buy their product as the thing most needful, the German Kali Syndicate urging potash upon the farmer as that for which his plants do most ravenously hunger, and the Chilean nitrate people pressing upon the bewildered husbandman his need of fixed nitrogen. That situation has improved somewhat, and at the time of the present writing, when there is a potash famine in the land, it is doubtful if very much phosphate or nitrate is offered as a substitute for potash. The mining and sale of phosphate rock is one of the great industries of the United States.

The old-fashioned sulphur matches were made by dipping the sticks first into molten sulphur and then the tips into a paste containing yellow phosphorus, an oxidizing agent and a gum to protect the phosphorus from the air and to keep the mass together. Enough heat was generated by rubbing the tip against any rough surface to start the reaction between the phosphorus and the oxidizing agent (manganese dioxide, for instance), and that in turn set fire to the sulphur, which ignited the wood. But not only was the fire danger of these matches very great: the yellow phosphorus is a nasty poison; the men who worked in the industry got "phossy jaw," and died of it, and now the manufacture of such matches is forbidden by law. The new kind of "strike anywhere" matches have a tip of phosphorus sesquisulphide in place of the yellow phosphorus. From the structure of these

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matches, with the ignition surface spreading over the tip of the match instead of enveloping the end, the fire hazard is lessened.

Safety matches are made of potassium chlorate, powdered glass, rosin, glue, and coloring matter, with red or amorphous phosphorus on the sides of the box. It is a pleasure to record that the manufacture of matches, involving as it does the use of phosphorus, has changed entirely so far as it has come within the hands of certain great administrators. It is not many years ago that to work in a match-factory was a job that any man might dread. Phosphorus is a nasty poison, and its effects are cumulative and cruel. By the substitution of the sesquisulphide for elemental phosphorus the hazard to health and life is removed, and one large manufacturing company, having useful patents covering the process, presented its patents to the United States Government, so that any manufacturer of matches may use them. The health record of the company's own works is something to be proud of, and it enjoys the advantage of well-paid, satisfied, and loyal employees.

Rocks containing phosphates of calcium and phosphorus in other forms are very wide-spread and are often found where they are not wanted. For instance, when they are found mixed in with iron ores the iron-master is likely to become unfit as a member of society: You cannot make steel by the old Bessemer process unless the amount of phosphorus present is very slight, because phosphorus spoils the steel. In the open-hearth process more phosphorus can be allowed, as in this way it is boiled off. But generally speaking, phosphorus is to the metals as whisky is to man. It has its uses, but it can do all sorts of harm. A little phosphorus in iron or steel will make

## ARSENIC

it crystallize, and so it becomes brittle and generally unreliable. On the other hand, it is useful in certain alloys. Phosphor bronze, for instance, is an alloy of phosphorus, copper, and tin. It is very hard and firm, and is used in making axle bearings. But there is much more effort made to get phosphorus out of metals than there is to get it in.

There used to be a tradition to the effect that phosphorus was food for the mind, because there is a slight amount of it found in the brain. It was held that a diet of fish was especially to be recommended because phosphorus is also found in fish, and therefore that the aspirant after intellectual life should address himself to codfish, shad, and even bullheads and suckers. The element is indeed found in fish, but chiefly as calcium phosphate in their bones.

Arsenic behaves something like phosphorus in its reactions. Usually it has three hooks, but sometimes it has five, and it shows several allotropic modifications. It may appear as a gray, crystalline substance, and a good conductor of electricity, or it may take the form of yellow crystals, or of a gray, amorphous powder or a black powder. It combines with oxygen to produce oxides, and these with water form acids. With the halogens it combines every way possible, and nearly all of its combinations are poisonous. So is pure arsenic.

With hydrogen it forms two combinations, the important one of which is arsine,  $\text{AsH}_3$ . It is a gas, and smells like garlic, but no one is able to smell it in quantity for any length of time, for the very good reason that it is one of the rankest poisons there are, nearly as dangerous as prussic acid.

Arsenic is found in nature in a free state, as an oxide

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or "white arsenic," and in direct combination with metals as arsenides. From a chemical standpoint it is not very aggressive, and it would seem that its poisonous quality must be due to catalysis. It is found in slight quantity in many ores, but is usually distilled or sublimated off in the process of smelting.

Of its two compounds with oxygen, arsenious oxide,  $\text{As}_2\text{O}_3$ , or white arsenic, is the best known. It is used in glass-making to remove the color produced by the lower oxides of iron. It is also used in enameling, in calico-printing, for fireworks, to prevent boiler scale, for fly and rat poisons, and as a preservative for mounted birds and animals. Paris green is arsenite of copper ( $\text{CuHAsO}_3$ ), and is a beautiful green pigment that was at one time in popular use as a paint, for coloring wall-paper, etc., but it is such a vicious poison that its use is generally restricted in this respect. Farmers find it useful for killing potato-bugs. Arsenic in one form or another has long been a favorite medium of the poisoners, although the tests to detect it are among the most delicate known, the presence of the most minute quantities being capable of demonstration. So delicate is one test that sometimes the slight amount contained in the glass has been partially dissolved out during the analysis, and dire confusion has resulted. The careful analyst tests his apparatus for arsenic first.

As with many other poisons, one may grow accustomed to taking arsenic in increasing amounts until more than double an ordinary fatal dose is taken with impunity. The inhabitants of Styria eat it (white arsenic) to increase their endurance. They are said to be of fresh complexion and long-lived, but to die suddenly. It is occasionally given to horses in small quantities to improve the appearance of their coats,

## ANTIMONY

especially when a sale to some one living at a good distance away is anticipated.

In alloys with metals arsenic has a tendency to make them brittle.

Antimony belongs to the same group as arsenic, phosphorus, and nitrogen; it has sometimes three hooks and sometimes five; it has three allotropic modifications—it appears as a crystalline, silvery-white, brittle, metallic substance, and as a yellow, and as a gray powder. The last is known as “explosive antimony,” and when heated or struck or scratched it changes into the crystalline form, increasing in density and with great heat.

It is found in small quantities in a free state in nature, but usually as an oxide or in combination with sulphur, arsenic, and the metals. The most common form is the sulphide, called stibnite,  $\text{Sb}_2\text{S}_3$ .

It makes, in a general way, combinations similar to those of phosphorus and arsenic.

In alloys with metals it has the general feature of making them brittle and hard, but it has the added peculiarity of expanding, like water, as it passes from a molten to a solid state. In castings, therefore, a very sharp impression is produced, and its value in type-metal can be readily understood. Type-metal is composed (subject to a considerable number of variations) of about 50 per cent. lead, 25 per cent. antimony, and 25 per cent. tin. Babbitt metal for bearings is, according to one recipe:

7.4 per cent. antimony; 88.9 per cent. tin; 3.7 per cent. copper.

Britannia metal is 90 per cent. tin and 10 per cent. antimony.

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With copper a brittle metal is produced by alloys of increasing proportions of antimony, ranging in color from copper red to rose red and from crimson over to violet. The violet metal is an alloy of half copper and half antimony.

In medicine we find antimony used in tartar emetic. This is a double salt with potash and a radical of antimony and oxygen as the two bases in combination with tartaric acid. The chemical name for tartar emetic is potassium antimonyl tartrate, and the formula is  $K$



There are five elements in the nitrogen group, and bismuth is the last of them.

	Nitro- gen	Phos- phorus	Ar- senic	Anti- mony	Bis- muth
Atomic weight: . . . .	14	31	175	120	208
Specific gravity: . . . . (Water = 1)	0.88	1.8-2.1	4.7-5.7	6.7	9.8
Melting-point: . . . . .		44°	500°	430°	208°

By the time we reach bismuth we have a real metal. Its combinations with oxygen are bases, not acids, and it is found chiefly in a native state. It looks very like antimony, but it does not appear to be poisonous. We might say that bismuth is the old man of the family, and that he had outgrown the poisonous quality that begins with phosphorus, is at its peak in arsenic, and decreases in antimony. It is used chiefly in making alloys, and in the form known as bismuth sub-nitrate it is used in medicine as an astringent and anti-septic dusting-powder.

## XI

### THE ALKALI METALS

Sodium and Soda—What It Is. Not—Frequency—The Chemical Old Mare—Its Thirst—Salts and Their Uses—Manufacture—Le Blanc—Solvay, Who Rescued Brussels—The Electrolytic Process—Potassium and Potash—Plenty of It—Prospects of Catching It—How Trees and Plants Refuse to be Deceived—The Legend of the Tree Brought up on a Bottle which could not be Weaned—Compounds—Lithium—The Rest of the Family

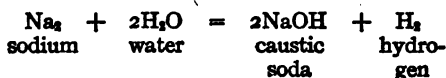
THE most frequent sign of soda that meets the American eye—being the inviting legend displayed by apothecaries and confectioners—does not indicate soda at all. “Ice-cold soda-water” is water charged with carbon dioxide,  $\text{CO}_2$ . It obtained its name by the old method of dissolving sodium bicarbonate in water and then liberating the gas by a mild acid such as cream of tartar. Such a preparation is now known as “Seidlitz powders,” whereas the old name holds to the water which has the bubbles but not the soda.

About  $2\frac{1}{4}$  per cent. of the crust of the earth is sodium, which makes it rank seventh in point of quantity among the elements. It has one hook, and is found chiefly as the chloride, which we have already considered under salt in connection with chlorine. It is also found as the nitrate  $\text{NaNO}_3$  in Chile saltpeter, as the sulphate  $\text{Na}_2\text{SO}_4$  in Glauber’s salt, and as

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the carbonate in the alkali deserts. In cryolite, or the ice stone of Greenland, it is found as a sodium aluminium fluoride. It is found in countless silicates, and, as a result of rock decay, it gets into the soil and so into animal organisms. Its end product in natural processes is salt, and its habitat the sea.

Sodium is not found in a free state in nature, because the pure element, which is a light, silvery, white-colored, waxy metal, combines immediately with water to produce sodium hydrate or caustic soda:



To prepare metallic sodium this process is reversed, practically, with the aid of the electric current. We say:



In practice it isn't so easy. Caustic soda is heated in a tank through which an electric current passes. The metallic Na formed at the cathode is kept away from the anode by an iron net. At the anode, OH groups are liberated which yield water and oxygen, or  $2\text{OH} = \text{H}_2\text{O} + \text{O}$ . The oxygen escapes, but the water goes back to the other pole, meets the metallic sodium, and produces caustic soda again:



As a result, the maximum yield for a given quantity of electricity is only 50 per cent.

This lust of sodium for water may be easily shown by cutting with a knife a little piece of metallic sodium from a bar and throwing it into a pail of water. It



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will swim around on the surface, generating hydrogen, which escapes, and producing a solution of caustic soda in the water. It is well not to stand too near, because it sputters, and nobody cares to have a piece of sodium busy with water or moisture, or even a solution of caustic soda, in his eye or on his countenance.

Metallic sodium is used in metallurgy, and is kept under kerosene or in some liquid which contains no oxygen. It is in the form of the carbonate as soda or soda ash, as it is called,  $\text{Na}_2\text{CO}_3$ , and as the bicarbonate  $\text{NaHCO}_3$ , and as lye or caustic soda or sodium hydroxide,  $\text{NaOH}$ , that it finds its great use. Note, please, that sodium bicarbonate is really a kind of half-carbonate, in that to one radical of the carbonic acid we have one sodium and one hydrogen atom, whereas in the carbonate or monocarbonate there are two Na atoms. We said, in considering sulphuric acid, that if it were called the old horse of chemistry, we should have to regard soda as the old mare. It is the grand universal alkali, and it is used everywhere, constantly. A few of its uses are given in *Chemistry of Common Things*, by Sadtler, elsewhere referred to, from which we shall copy:

<i>Salt</i>	$\text{NaCl}$	Used: Condiment. Chemicals.
<i>Sodium hydroxide</i> (Caustic soda, lye)	$\text{NaOH}$	Soap. Chemicals.
<i>Sodium carbonate</i> (Soda ash, sal soda, soda crystal)	$\text{Na}_2\text{CO}_3$	Cleaning. Soap powders. Chemicals. Scouring.
<i>Sodium bicarbonate</i> (Cooking soda)	$\text{NaHCO}_3$	Baking powders. Chemicals. Medicine.
<i>Sodium sulphate</i> (Glauber's salt)	$\text{Na}_2\text{SO}_4$	Glass-making. Wood pulp. Medicine.
<i>Sodium phosphate</i>	$\text{Na}_2\text{HPO}_4$	Medicine.
<i>Sodium monophosphate</i>	$\text{NaH}_2\text{PO}_4$	Baking powder (Ryzon).
<i>Sodium triphosphate</i>	$\text{Na}_3\text{PO}_4$	Softening water.

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<i>Sodium thiosulphate</i> (Sodium hyposulphite)	$\text{Na}_2\text{S}_2\text{O}_3$	Used: Tanning and photography.	
<i>Sodium nitrate</i>	$\text{NaNO}_3$	Agriculture. Chemicals.	
<i>Sodium borate</i> (Borax)	$\text{Na}_2\text{B}_4\text{O}_7$	Cleaning. Mild alkali.	
<i>Sodium silicate</i> (Water glass)	$\text{Na}_2\text{SiO}_3$	Soap-filling. Bandages. eggs.	Silk-dyeing. Preserving
<i>Sodium chlorate</i>	$\text{NaClO}_3$	Pyrotechnics. Textile work.	Explosives.
<i>Sodium peroxide</i>	$\text{Na}_2\text{O}_2$	Bleaching.	
<i>Sodium dichromate</i>	$\text{Na}_2\text{Cr}_2\text{O}_7$	Tanning.	

And this is only a hint of its many uses. Making soda is one of the leading chemical industries and the process always starts with salt. The old standard method of producing it was that of Nicholas le Blanc, the domestic physician to the Duke of Orleans, who in turn provided capital for the start of the industry. The French Revolution came along and left poor old Doctor le Blanc stranded, while the industry, as industries have a way of doing, quietly moved over to England.

This is a great trick of industries which are not interested in political economy or human welfare except as it may affect production. At the time of this writing there is a movement of electrochemical industries from Niagara Falls, where they started, to Norway, where there is cheaper power and more of it. Whether we shall continue to waste our precious power by permitting the continued waste of the wicked beehive coke-ovens, which burn up everything except the coke produced and do not even conserve the power that goes to waste; whether Niagara Falls will be turned over entirely to industry or not; whether our conservation laws in the United States will be modified so as to permit the profitable industrial use

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of available water-power sites—are all questions that are in the air, and, while they are in process of settlement, the electrochemical industry will probably settle down somewhere and take a lead for fifty or a hundred years.

The Le Blanc process consisted in treating salt with sulphuric acid, thus producing sulphate of sodium,  $\text{Na}_2\text{SO}_4$ , or salt cake, as it is called. This was heated with coal and limestone (calcium carbonate) until the mass had fluxed, when the reaction took place. This brought the carbonic-acid radical over to the soda, and the sulphuric acid produced sulphate of lime or gypsum. The alkalies changed acids in the process. That is the reason why the soda, being obtained from the flux, obtained its name of soda ash. In the first process of making salt cake, chlorine was liberated, which was conserved as hydrochloric (or muriatic) acid,  $\text{HCl}$ , and it was also used to make bleaching-powder, which is obtained by passing chlorine through a series of chambers containing slacked lime. The Le Blanc process is now nearly obsolete.

In 1861 Ernest Solvay, of Brussels, patented the Ammonia Process, which is that by which the major portion of the soda used to-day is made, although we shall soon note another process, one that is crowding it whenever there is sufficient power available for electricity.

In the Solvay process, common salt,  $\text{NaCl}$ , is treated with ammonium bicarbonate, or successively with ammonia and with carbonic-acid gas, at a low temperature. Sodium bicarbonate and ammonium chloride are formed, and the sodium bicarbonate, being nearly insoluble in a solution of ammonium chloride,  $\text{NH}_4\text{Cl}$ , it precipitates out. The mother liquor is drawn off, treated with caustic lime, which frees the

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ammonia,  $\text{NH}_3$ , and produces calcium chloride. The  $\text{NH}_3$  is saved, and the calcium chloride is waste, or nearly so. It is used to keep dusty roads moistened, because it draws water from the air. It is also used to make anti-freezing mixtures, but if any one will discover a steady use for large quantities of it he will have no trouble in getting invitations to dinner. Instead of using lime, it is possible to employ magnesia. From the magnesium chloride the chlorine may be regained by heating, and the magnesium oxide or magnesia, which is formed as soon as the chlorine leaves it, may be used over and over again.

The bicarbonate of soda is changed to the carbonate by heating, and caustic soda,  $\text{NaOH}$ , is made by treating the carbonate with quicklime. It was Ernest Solvay, who had amassed great wealth from the soda industry in Europe and America, who paid the vast indemnity demanded by the German invaders as their price for not destroying the city of Brussels.

A still newer method, originating in America and developed by various American chemists, is the electrolytic process. It is not so simple as it looks, but in effect the salt brine is led into an electrolytic cell. A current of electricity is passed through which splits the  $\text{Na}$  from the  $\text{Cl}$ , each element going to its respective pole. The sodium combines with the water to produce caustic soda, as described in the beginning of this chapter, and the chlorine is saved, compressed, and cooled until a liquid condition is reached, and is then sold to bleacheries and to chemical works for chlorination processes and for the destruction of bacilli in city water.

Potassium ( $\text{K}$ , for the Latin word *kalium*) is the elemental or metallic potassium, while potash is the

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common term for the carbonate. The nomenclature, however, is a little loose, and "potash salts" is used to indicate salts of potassium, but chiefly the chloride. It is a very close cousin to sodium. It has also only one bond, and in a metallic state it is soft, waxy, of a silvery-white color, and changes over to the hydroxide or caustic potash, KOH, on being brought into contact with water. Indeed, a piece thrown into water will dance about, liberating hydrogen and casting caustic potash into solution at such a lively rate that enough heat is generated to set the hydrogen afire.

Potassium is not found in a free state in nature, for the obvious reason that it will not remain free, but it is very wide-spread. In the form of nitrate,  $\text{KNO}_3$ , or saltpeter, it was formerly found in deposits in India, but these have long been exhausted. They were by no means so extensive as the Chilean beds of nitrate of sodium. The great source of supply has been in the deposits of Germany, in Hanover, Westphalia, and in Alsace, and at the time of the present writing there is a serious potash famine in the United States.

The situation reminds one of the old line about "Water, water everywhere, and not a drop to drink," because there is any amount of potassium to be found in this country. The greatest supply is in the wide-spread mineral called feldspar, which contains up to 17 per cent. K, but, alas! it is bound up with aluminium as a double silicate, and it is insoluble. That is to say, the potash is there in the feldspar, but it is in the form of glass and pottery. So far, the only way to get it out is by the heat of the electric arc, and that takes great quantities of cheap power. This problem is sure to be solved some day; there are patents by the hundred on various processes to do it.

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But no large plant of importance is in operation yet, nor is there, so far as we know, any in process of construction at this time. As we have said before, the American business man does not like to spend money on experiments, and every one of these processes requires factory demonstration to prove itself. And yet, so hopeful are men of the solution of this riddle that a syndicate of miners in Colorado are, at the time of this writing, setting aside daily two thousand tons of finely ground and washed feldspar against the time when somebody will appear with a successful process. There is some potash in sea-water, and the giant kelp of the Pacific coast absorbs it, so that it contains from 10 to 40 per cent. of  $KCl$ . Several large works are in process of construction in California to secure the needed potash from this giant seaweed, but these will produce only a very small fraction of the potash needed. A very interesting suggestion was lately made by a well-known chemical writer. He was visiting California, and observed the great activity in building plants for the commercial recovery of potash. Here are these big seaweeds, thought he, which take up a great deal of potash from the very small amount held in solution in the ocean. The plants do not take in sodium salt, of which there is a much greater amount in the sea. The separation is accomplished by some kind of semi-permeable membrane which lets through potash salts and iodine, but keeps the soda salts out. "What kind of a membrane is it?" he asked. "What is the character of the semi-permeable diaphragm, or, generally, what is the mechanism of the concentration process?" Here is another nut to crack in physical chemistry. If the nature of the process by which the giant kelps take up the potash salts and leave the compounds of sodium

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behind were known, we could put tanks with walls of such a nature into the sea and enjoy watching them fill themselves with pure solutions of potash. Then we might concentrate the liquor, crystallize out the potassium salt, dry it, sell it, and send for another box of those fifty-cent cigars. It seems likely, though, that even if we knew how to turn the trick, it would only work with dilute solutions. Then the cost of concentration might be too great for us to buy the cigars, after all.

Another source of supply is in the saline deposits of dry lakes in southern Utah and California. These are being operated in a small way, but not nearly enough for our needs. It is said to cost the German syndicate about \$20 a ton to mine and prepare the muriate of potash for market, and they get about \$40 a ton for it. Or, rather, that was the case before August 1, 1914. Since then as high as \$450 a ton has been paid for it.

Trees and plants must have potash. The clearest evidence that trees need it is the amount of it we find in wood ashes, in which it runs as high as 5 or 6 per cent., despite the fact that some of it goes up in smoke. Indeed, that is where it got its English name—the ash from under the pot. Then, to be 'scruciating elegant, we have Latinized the word to potassium. The Germans stick to the word that came from the Arabic alchemists, and call it kalium, which is related to the word alkali.

Just what rôle potash plays in the nutrition of plants it is hard to tell. It used to be so simple to think of soil as consisting of so much clay (silicate of aluminium), so much sand (silica), with so much fixed nitrogen, potash, and phosphates, and nothing else. The idea was that after the chemist had done a

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little fuddling with it and made his analysis, the enlightened farmer would know exactly what to do. Things are so easy when we know only a little! Now the chemist does rightly and properly analyze soils, and the enlightened farmer is greatly helped by his results, but remember, please, that agriculture comes more properly under the head of plant physiology than under chemistry. The soil teems with life. In summer from half a million to a million bacteria are found in a single grain weight of soil. Besides bacteria, it has yeasts, molds, fungi, protozoa, amoebæ, nematodes, and worms. Then there is humus, which is fermenting organic matter. The nature of soils is one of the most complex of studies. There is, however, a gross chemical aspect of soils which is the basis of the fertilizer business, if not of the use of fertilizers, and this we shall consider. We have discussed the need of fixed nitrogen, and we know the need of phosphoric-acid salts. What potash seems to do in the economy of plant life is to act as a catalyst in that marvelous synthetic laboratory in the plants which mates up carbon dioxide and water to sugar and starch and then to cellulose. The richer plants are in carbohydrates (sugars, starch, etc.) the more potash they seem to contain. It seems to aid in the growth of strong, vigorous roots and stems, and in neutralizing plant acids it appears to affect favorably the flavor of fruits. It is claimed also that plants become more resistant to disease if adequate potash is supplied. The reason why sodium may not be substituted for potassium in plant economy is possibly because the potash salts diffuse more readily through the cells than those of soda, or because of the greater liking that potash salts have for water than soda salts. The fact is, however, you cannot substitute soda for potash



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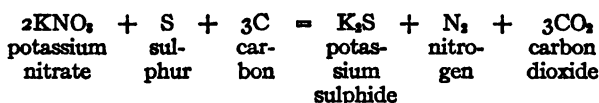
in agriculture with success—so far. The plants will discriminate.

The natural history of potash is like that of sodium. It exists principally in the silicates, in feldspar and mica especially, and upon the decay of these minerals some of it is carried into the soil and thence to plants. They must have considerable of it for lusty growth, and, as we have intimated, many kinds of vegetation seem to need it for flavor. The legend is told by a gentleman with a lively imagination of a farmer who had a wonderful apple-orchard in which everything was done which science could provide for his trees. Finally, on the ground that a tree is, after all, only an osmotic engine, the lord of the orchard bethought himself that he could give the needed fertilizer to one of his trees by bringing the constituent parts of the needed manure or "tree food" into its circulation from a solution contained in a bottle and fed by gravity through a gimlet-hole. The tree took by gravity through the gimlet-hole far more than its sluggish roots would absorb, and its carefully balanced rations of salts in solution soon began to show results. In size, taste, and quality they outshone any apples ever grown, but, alas! when cold weather came the tree had grown so accustomed to being fed by the bottle that its roots had atrophied, and the farmer was unable to wean it. We do not know the fate of that tree—whether it turned out well or badly, and we never have brought ourselves to believe in it thoroughly. We fear it was cut off in the blossom of its youth.

The compounds of potassium are so analogous to those of sodium that we shall not mention them in great detail. The chloride and sulphate are used for fertilizer materials, the bromide is used as a medi-

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cine, largely for its sedative effect, and the iodide, like sodium iodide, is used also in medicine. The fluoride has the peculiar quality of forming the double halide FK, FH; and the cyanide, like the cyanide of sodium, is used to extract gold from its ores. The nitrate,  $\text{KNO}_3$ , is one of the constituents of gunpowder in the proportion 75 saltpeter or  $\text{KNO}_3$ , 10 carbon (charcoal), and 15 sulphur. When it explodes this is about what happens:



This is not entirely correct, because the remaining potash is not all in the form of  $\text{K}_2\text{S}$ . But the gases are chiefly  $\text{CO}_2$  and some  $\text{CO}$ . The tension of the gaseous products is about 6,500 atmospheres (96,000 pounds to the square inch) and the temperature about  $2,200^\circ$  centigrade.

The silicate of K is very like Na silicate. The sulphides are not very stable and oxidize easily.

Lithium, sodium, and potassium constitute the principal members of the group known as the alkali metals, and lithium is the first of the series. None is found free in nature, all are widely distributed, but lithium is found only in small quantities. It occurs chiefly as the silicate in lepidolite or lithia mica, as the phosphate in triphylite, and in company with Al, Na, and Fl in amblygonite. Finally it is met with in the ashes of certain plants, such as tobacco, showing that it is contained in the soil. Minute traces of it are found in many minerals.

Metallic lithium, prepared by electrolysis of the

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fused chloride, is the lightest of all solid substances except frozen hydrogen. It is but little over half the weight (less than six-tenths) of water, and it floats on kerosene. It is silvery white, but tarnishes rapidly on exposure to moist air. With oxygen it produces lithium oxide,  $\text{Li}_2\text{O}$ , and this goes over into the hydroxide,  $\text{LiOH}$ , which dissolves in water, producing a strongly alkaline solution, like caustic soda,  $\text{NaOH}$ , or caustic potash,  $\text{KOH}$ .

The chloride,  $\text{LiCl}$ , is very soluble and takes on water from the air.

The carbonate,  $\text{Li}_2\text{CO}_3$ , is not very soluble in water, in which it differs from the Na and K carbonates.

The phosphate,  $\text{Li}_3\text{PO}_4$ , shows the same peculiarity.

Lithium salts are used in medicine. There is but little if any technical use for the metal or its compounds at present.

The other two members of the family are rubidium and caesium, which we shall not consider further than to note that they are also soft, silvery-white metals, and we mention them only to show the family relation, how they progress up in one respect and down in another, just like some other families of elements:

	Lithium	Sodium	Potas- sium	Ru- bidium	Cæsi- um
Atomic weight.....	6.94	23.0	39.10	85.45	132.81
Specific gravity..... (Water = 1)	0.534	0.971	0.862	1.532	1.87
Melting-point.....	186°	97°	62°	62°	26°
Boiling-point.....	1400°	877°	700°	696°	670°

## XII

### SAND AND CLAY

The Enormous Supply of Silicon—Its Inert Ways—The Silicon Man—Glass History—The Cautious Venetians and the Glass-makers Who Stepped Heavenward—Kinds of Glass—Coloring—Boston's Purple Windows—Glass-making in the United States—The Art of It—Aluminium—The Young Fellow of Twenty-two Who Made It—The Frenchman Who Did the Same Thing—Value of Backing by Pittsburgh Millionaires—Clay—Brick—Pottery—Glaze—Different Kinds of Clay—Feldspar—Fuller's Earth—Mica—Note on Boron and Borax

ABOUT 50 per cent. of the solid crust of the globe is oxygen, and about 25 per cent. of it is silicon. But silicon is not found in a free state in nature; it is too fond of oxygen. It belongs to the same group as carbon, and has, consequently, four hooks to the atom. It can be driven from its combinations in the laboratory without great difficulty, but it burns back to silicon dioxide, or silica,  $\text{SiO}_2$ , at a comparatively low temperature.

In a pure state it is known in three forms: as a brown amorphous powder, as graphitoidal silicon (in black flakes), and as crystalline (in dark, iron-gray crystals).

As silica,  $\text{SiO}_2$ , it is sand, and it constitutes from 20 to 35 per cent. of granite and primitive rock, and along with compounds of aluminium, which constitute clay, *it is the earth*.

It behaves like carbon in its combinations, except

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that it may be said to regard this world as a cold, bleak place, and it does not care for combining much except with oxygen. It *can* hook up its atoms together in chains, as carbon does, and the number of imaginable silicon compounds is beyond compute; but when the chemist with infinite pains has negotiated a number of silicon compounds that correspond to those of carbon, such as, for instance, silicon chloroform,  $\text{SiHCl}_3$  (chloroform being  $\text{CHCl}_3$ )? and similar bodies, they disintegrate on contact with water or in the air and the silicon atom will yoke itself up with oxygen again to  $\text{SiO}_2$ . It may be livelier at high temperatures, but that is just where we cannot follow it. Perhaps we can get a better idea of this feature of the nature of silicon by quoting some verses called "The Silicon Man," which appeared several years ago in *The Percolator*, issued by the Chemists' Club of New York. The verses will hardly stand alongside of the rhapsodies of Milton, which are occasionally quoted in popular treatises on chemistry; indeed, their feet are so shaky that they can hardly stand at all; but they may throw a little light to the chemical imagination as to what silicon would do if it only had the temperature—and the audience.

### THE SILICON MAN

I saw a glowing Silicon Man  
Within my chamber fire,  
And heard him cry in agony,  
"More fuel, or I expire!"

So from the wood-pile I brought in  
Some pine and hickory,  
And as I fed it to the flames  
He straightway piped his eye.

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"I am," said he, "John Silicon,  
And I am so constructed  
That Silicon's my substitute;  
My carbon's all deducted.

"My tissues, nerves, and viscera  
Show this phenomenon:  
That just as you of carbon are,  
I am of silicon.

"In other features we're the same  
(More fuel! The coal flame twinges!)  
The point is that our molecules  
Are different in their hinges.

"You call those things organic which  
By nature are based on  
Some carbon atoms—more or less—  
We hold to silicon.

"At temperatures such as you know,"  
Said he, "we freeze. We turn  
To consciousness again when you  
Would sizzle up and burn."

Now this peculiar Silicon Man  
(The fire was bright as gold)  
Seemed suffering, and so I gave  
Him whisky for his cold.

He liked it; said he never felt  
So well as when he had  
A taste of liquor on his tongue;  
It was his little fad

To make an ethyl silicohol  
By substituting Si  
For carbon in the alcohol;  
He called it Hades Rye.

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The Silicon Man drank more and more,  
He grew full talkative,  
And drank the substituted dram  
As though he were a sieve.

He said he'd lived, lo, many a year—  
An old, old man was he—  
And yet he had not lived so much,  
Because, as you can see,

At ordinary temp'rature  
His soul was frozen dead,  
And only resurrected when  
The flames were blazing red.

"This life," said he, "is not so bad  
When once you're used to it:  
To freeze whene'er the fire goes out  
And waken when it's lit.

"The orthodox concept of hell  
Is partly right," said he,  
"The heresy lies in the claim  
That heat is misery.

"My needs," said he, "are very few;  
I want no meat nor bread,  
And if you feed the fire well  
You'll never find me dead."

But when at last my bedtime came  
I heard a painful shout;  
It was a cry for silicohol  
Just as the fire went out.

We need not worry much about the organic silicon compounds. There are a number of stable ones found in nature—grains need it in their stalks, and the

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feathers of birds and the scales of fish carry them. But the great mass of it is in the form of silica,  $\text{SiO}_2$ , and as such it is found in various forms. It is found in a fine state of division consisting of the scales of extinct diatoms, and known as kieselguhr, or diatomaceous earth. This is used for filtering, in the preparation of dynamite, and other purposes. Then we find it as quartz in crystals, and in another crystalline form as tridymite in porphyry and other rocks, and in a quasi-amorphous state with water locked in as in opals. It melts to a colorless glass, is insoluble in water, and is not attacked by acids except hydrofluoric. The amorphous silica is soluble in alkali if in a finely divided state, but, when fused, alkali only attacks it slightly. Silica is the anhydrid of an acid which would naturally be obtained by adding water, except that pure silicic acid as such is not known in a free state. But its salts are known. Many silicates are prepared artificially.

Silicates of soda and of potash are soluble in water; other silicates are not.

By bringing sand and salt ( $\text{NaCl}$ ) and coke together and heating them in an electric arc, Acheson produced a crystalline body composed substantially of the two elements, or carbide of silicon,  $\text{CSi}$ . This is well known as carborundum, and is made at Niagara Falls. It is so hard as to scratch rubies and is not acted upon by acids at ordinary temperatures. It is one of the hardest abrasives, and has found wide use as a substitute for emery. There are silicides of many metals, but their relation to iron and steel we shall discuss when we come to the iron and steel industry.

The most extended use of silica,  $\text{SiO}_2$ , in industry is in glass and pottery making.

Glass is a solid solution of indefinite composition,



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produced by the fusing of sand (silica) with the oxides of two or more metals. It has no definite molecular structure like a crystalline substance; its component parts present the same indefinite arrangement as is found in a solution. Glass has the property of being transparent and rigid at ordinary temperatures, but plastic when heated. Its properties change according to its composition, and, while we may say, generally, that it is insoluble, this is only approximately true. Acids affect it (always excepting hydrofluoric acid) less than alkalies, but even water, especially under high pressure and high temperature, will corrode some glass.

Glass was made as far back as 1400 B.C., and at the dawn of the Christian era it was a thriving industry. It degenerated in medieval days, chiefly because the natron, or natural sodium carbonate which the Romans used, was no more availed of, and impure wood ashes were used in the place of it. The Venetians kept up the quality of their product by using the ash of a sea plant which they called kali for their base. In the palmy days the Venetians would not let a man escape from the country if he knew how to make glass. If he did, they followed him up, and if they found him he was supposed to have a harp by the time they finished with him.

If sand, which is nearly pure  $\text{SiO}_2$ , could be melted with ease, it would be ideal glass—quartz glass—but it is too hard to fuse. So the maker adds fluxes. As soon as you add soda to the sand, down comes the melting-point of the mixture, and soda is the most convenient flux. But when the glass is made, the less soda you have in it the better the product is likely to be, for silicate of soda is very soluble. Then, too, the more soda glass contains the more will it expand and

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contract in heat and cold—and so be likely to break—and the lower is its tensile strength. To overcome the solubility another base is added, and this is usually lime. Not always enough lime, however, because the more lime the glass-maker puts in the more fuel he needs for melting, and sometimes he is of an economical turn of mind. Then, too, sometimes the buyer wants his window-glass or his bottles a little cheaper than he has a right to ask for.

If a more brilliant and denser glass is wanted, lead oxide is added, and the lead becomes a silicate.

If potash is used in the place of soda, the differences are marked. For instance, a vessel made of lime-soda glass without enough lime in it becomes covered in time with a whitish powder which leaves the glass rough. That is, the soda oozes out and by exposure to the air becomes carbonate of soda, which is a whitish powder. Potash glass without enough lime will also sweat out potash, but the carbonate of potash as formed draws on water from the air and so runs off without injury to the surface of the glass. Potash glass has a bell-like ring which soda glass has not, due to greater elasticity, and this makes it more desirable for tableware. Generally speaking, potash glass is cleaner and brighter.

Cut glass is a potash-lead solution; but there being no potash available in the United States these days, it is made with soda, and it is hardly likely to stay as bright as if it were made as before. On the other hand, by that strategy which constitutes research, a better electric-light bulb has been produced with soda than was formerly made with potash.

Laboratory glass is now made in the United States in large quantities, and the problem is similar to that for making glass kitchenware—for, if we but knew it,

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every kitchen is a laboratory. The product must have a low coefficient of expansion and high tensile strength. That is, it must not expand and contract too much with heat and cold, because if, say, hot water is poured into a vessel it will expand where the hot water is, but not above it, and there comes the breaking strain. And its tensile strength should be high, so that if you drop it on the floor it will hold together with sufficient tenseness and not break. The glass-maker lowers the coefficient of expansion by adding boric oxide, and he adds silica and aluminium to increase the tensile strength. Here are a number of kinds of glass and their special uses:

Silica, with soda and lime or soda-lime glass. Used for window-glass, chemical glassware, and bottles.

Silica, with soda, lime, and aluminium. Used for beer, wine, and spirit bottles, owing to strength and insolubility.

Silica, with potash and lime. Bohemian glass, for tableware.

Silica, with potash and lead. Flint glass, tableware, optical goods.

Boro-silicon, with soda and lime. Optical goods, thermometer tubes, and laboratory ware.

Boro-silicon flint, with potash and lead. Optical goods, enamels, imitation gems, etc.

Borate and phosphate glasses, containing no silicon, for certain optical purposes.

Quartz, pure. Does not obstruct the passage of ultra-violet rays as does all other glass, and is not broken or cracked by sudden changes of temperature.

Glass baking-dishes are coming into use, first, because they can now be made, and, second, because

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baking takes place much more rapidly in these than in metallic pans. The reason is simple when you know it—metal reflects 83 to 99 per cent. of the radiant heat that strikes it, while glass reflects only 3 to 14 per cent.

The soluble silicate of soda is called "water glass," and is used for making bandages for broken limbs, and for keeping eggs and other purposes.

Glass is colored by means of certain metallic oxides. Ferric (iron) compounds produce green color; ferrous compounds color it yellow. Manganese ranges from amethyst to violet color. The full effect is produced only when the manganese is fully oxidized, and this takes place on long exposure to the actinic rays of the light. Manganese is often added to window and other glass to correct the green color from iron impurities, and the violet color of arc-light glass is due to the oxidation of the manganese by long exposure to the light. The same phenomenon may be observed in old houses in Boston and in Amsterdam, Holland. Very slight quantities of cobalt make glass blue. Iron and manganese make it brown, and in excess make it black. Colloidal gold imparts a red color to it. So will copper if larger amounts are used, but it is very difficult to get certain results with copper.

In making glass it is always necessary to use some "cullet," or broken glass, which serves as a flux in the glass pots or tanks. When the glass is made there is always some scum, called "glass gall," that floats on the top. This is skimmed off, and then the temperature is allowed to cool down until the glass is ready for blowing or casting.

The principal product of the American glass industry is building-glass, of which there are three classes—sheet (or window), plate, and wire-glass.

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Four-fifths of the window-glass made here is mechanically blown, while up to the present time plate-glass is always cast. In the near future, however, owing to improvements, plate-glass will also be made by means of blowing-machines. The difference between plate-glass and sheets is of a mechanical rather than a chemical nature. Wire-glass is applied in structural work, requiring a material of great strength; it is especially useful in factory construction, owing to its resistance to shock and its fire-retarding qualities.

In addition to building-glass there is a great pressed and blown hollow-ware industry. This includes the tableware, kitchenware, and bottle industries. Bottles of all sizes, from vials to carboys, are now blown by machinery. The development of the automatic bottle-machine revolutionized the industry.

Not long ago a friend asked me why we imported so much table glassware, the finer sorts being almost entirely of European make. The answer is simple—we haven't the skilled labor. But the reason why we have not the skilled labor is far from simple. Let us see, however, if we cannot make a guess at it. When a man achieves sufficient skill to make glassware of exceptional beauty he must have sufficient taste to know the difference between that which is good and that which is not good; he must be enough of an artist to sense beauty when he has it before him. If he is only a hand in a factory, with more interest in his hours and his pay than he has in the individual quality of his work, he can turn out good, standard designs, fair enough for anybody to use, but he will not, because he cannot, under the circumstances, make exceptional wares. To make these requires an artist, and the artist, with his discriminating taste, finds delight in the thing of beauty and distress in that which

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lacks it. He enjoys his work more than the ordinary worker, and he suffers more over it. One day is not at all like another. In making glass, for instance, he has more than a job; he has a profession. Just as the physician likes to succeed with a difficult case and is disappointed if his methods fail, so this artist worker gets nervous over his task and has his good days and bad ones. He wants good pay, and he gets it, but he wants a great deal more. He wants to speak his own language, he wants to select his own friends, he wants to hear his good work praised, for comfort's sake, and he wants friendly criticism from his fellow-craftsmen. The chances are he has never heard of sanitary plumbing, but it is still more likely that he tends a little flower-garden and has a favorite spot of green grass where he likes to lie down of a late summer afternoon. He takes himself very seriously and expects others to consider his individuality. He may be especially fond of a local brew of beer or a *vin du pays*, both of which may injure his health, but it is impossible to persuade him that it is so.

That seems to me to be the reason why we keep on importing. At the same time I think it fair to say that in cut glass the product of the United States is equal to that of any country when the makers can get potash to make the quality desired. The work of cutting, however, is more mechanical and less artistic than required to produce other ornamental glass objects. Some day our ornamental glassware may equal that of France, Saxony, or Bohemia. This will be when we learn how to deal with the artistic temperament. To the man with a love for organization and a sense of order the artistic temperament offers problems to rack his very soul.

Now let us return to our chemical muttons.

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Aluminium or aluminum, as it is often called, is a metal in nearly every respect except that the hydroxide dissolves in alkalis to form aluminates, thus acting as a very mild acid. It is the third of the elements in the way of abundance in the crust of the earth. It is not found in a free state, owing to its affinity for oxygen, and until the hydro-electric development at Niagara Falls it was too expensive to prepare to find general use. This "silver from clay," as it has been called, is now produced in enormous quantities at Niagara Falls by the process of the late Charles M. Hall, which he worked out in 1886, a year after he graduated from Oberlin College, when he was twenty-two. Heroult, a Frenchman of about the same age, and also a brilliant metallurgist, devised the same process at about the same time in France, but Hall had the advantage of a little time, certain practical details, and the further convenience of backing by some Pittsburgh millionaires. So Hall had the pleasure of seeing, within the short span of his life, the price of aluminium fall from four dollars a pound in 1886 to eighteen cents a pound, and of being the man who made it happen. He died at the age of forty, leaving a fortune of many million dollars. Heroult, after Hall's success, addressed himself to the development of the electric-steel furnace. He was well known to American chemists from his frequent visits to America, and was as joyous and agreeable a companion as one is likely to meet. He died shortly after Hall.

Very fine particles of aluminium will burn to the oxide called alumina,  $\text{Al}_2\text{O}_3$ , in an atmosphere of oxygen, but in bars, sheets, or wire it holds well in the air because of a thin film of alumina which is formed on the surface. This alumina is found in a mineral called bauxite, which contains 50 to 70 per cent.

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of  $\text{Al}_2\text{O}_3$ , and is mined in Georgia and Alabama and in France.

Corundum is practically pure alumina, and is one of the hardest substances. Emery is impure alumina, and contains magnetite and hematite; it is nearly black in color. Both corundum and emery are used as abrasives.

Now just as we found silica,  $\text{SiO}_2$ , to be the chief ingredient of sand, so silicate of aluminium is the chief ingredient of clay. There is an aluminium chloride,  $\text{AlCl}_3$ , which is an unstable compound, but which is used in organic chemistry. Among its various applications it is found useful in separating gasoline from heavier bodies in crude petroleum.

Aluminium sulphate, in the form of a double salt with an alkali, will crystallize with a great deal of water in the crystals. These bodies are called alums. Ordinary alum, that we know as a mild astringent in household use, is potassium alum. In the dyeing industry this is being superseded by aluminium sulphate and sodium aluminate.

The Hall process requires alumina for the manufacture of metallic aluminium. Indications point to the discovery of a more economical process whereby the metal will be obtained direct from the silicate, or clay. Clay is the generic term for that kind of earth composed chiefly of silicate of aluminium. It is never pure; it is mixed with silica, and, although a reasonably pure silicate of aluminium called kaolin is white, there are not many white clays. Organic matter, humus, fossils, shells, limestone, iron as sulphide which makes it dark blue and which weathers to brown, and oxides of iron making it red and yellow, are some of the things found with it. And since clay, when finely enough divided, is in a colloidal state, and will slip



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through almost any filter, it is fair to say that the chemistry of clay products is full of difficulties.

Clay has the property of being soft, coherent, and plastic when wet, and when dehydrated one of the most indestructible of substances. Heat will not then disintegrate it, chemically, save at very high temperatures, and it does not take on water to go back to its original condition. The only trouble is, as every housewife knows, things made of clay will break.

To make brick, clay is shaped into forms and fired. There are refinements and difficulties in the handling of materials, but we shall not go into them. Fire-brick requires a clay very low in iron and rich in silica.

Pottery is a clay industry, and the number of kinds of clay employed in it is legion, but in effect this large number is due to the very many kinds and quantities of impurities there are mixed with aluminium silicate. To make flower-pots is no more of an art than making brick, but the refinements of the art reached by the great Chinese potters baffle the chemist. The trouble is, the reactions all take place at such high temperatures that Mr. Chemist cannot be there himself to find out what happens. If he could only turn into a "silicon man" and spend a season in a pottery kiln and a cement kiln, he would have enough material for any number of Ph.D. dissertations.

When clay is fired it becomes hard and brittle. But it is still porous. In order to avoid this porosity and to make it easier for the potters, quartz and feldspar are added. Now the less such admixtures are present the more difficult the porcelain is to burn, but at the same time the less sensitive the ware is to changes in temperature. The glaze is produced by a second firing, and the effect of the process is to cover the earthenware with a kind of glass. In com-

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mon pottery this is produced by introducing salt,  $\text{NaCl}$ , into the kiln. The hot steam causes the formation of hydrochloric acid,  $\text{HCl}$ , and sodium hydroxide,  $\text{NaOH}$ , which unites with the clay to form sodium-aluminium silicate—a common glass. Every type of potters' clay has its own type of glaze, say the potters, although with any good type of plastic clay which cannot be fired at the highest temperatures lead glazes have proved practicable. This is provided by lead oxide. Putting on the glaze is putting a coat of glass on a vessel.

The colors are applied sometimes before the first firing and sometimes afterward, but before glazing. They are mineral colors, of course, because the heat of the kiln would destroy the chemical constitution of organic compounds.

The principal varieties of clay are:

*Clay*, the term by which aluminium silicates are generally known, and applies to those not otherwise classified.

*Ball clay*, plastic and of high tensile strength, used in making porcelain and to give body, for instance, to abrasive wheels.

*China clay, or kaolin*, white, consisting almost entirely of hydrated silicate of alumina. Used in making chinaware, as a filler for cotton goods and paper, and in coating book and wall paper, cloth for window-blinds, in paint manufacture, and in some floorings.

*Fire clays*. These differ among themselves, but are low in impurities, such as lime, magnesia, iron oxide, and the alkalis which are fluxing materials. Used for fire-brick and other refractories.

*Pipe clay*, plastic, white, and relatively high in silica. Used in making porcelain and enamel-ware. Also

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used in paint-making as a depository for certain pigments. Must be free from grit.

*Slip clay*, applied to a clay used as a glaze for stoneware. Is high in fluxing impurities and melts to a greenish or brown glass.

*Stone clay*, usually refractory or semi-refractory, and vitrifies without losing its shape. Must have good tensile strength and be plastic enough to work on a potter's wheel. Used for the body of stoneware.

*Feldspar*. In discussing potash we referred to feldspar as an unlimited source of supply, provided only the potash could be removed from it. But the mineral has other uses, as you shall see. It is a very wide-spread mineral, although often found in such small grains mixed with other rock as not to be available. There are, however, many large deposits of it which may be easily mined and separated. The chemical composition is about as follows:

Silica ( $\text{SiO}_2$ ),	65	per cent.
Alumina ( $\text{Al}_2\text{O}_3$ ),	18	"
Potash ( $\text{K}_2\text{O}$ ),	17	"

The potash is sometimes partly and sometimes wholly replaced by soda. The spar is mined and ground usually in pebble-mills lined with quartz and using flint pebbles to avoid contact with iron, for the chief use of feldspar is in the ceramic arts, and the presence of a very small amount of iron will affect the color. In the body of porcelain it fuses during the firing and forms a firm bond between the particles of clay and quartz. In the glaze it fuses and forms with the other ingredients an opalescent, glassy covering. The melting-point depends upon the amount of alkalies (potash and

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soda) it contains; the more alkali the lower the melting-point, and as potash is replaced by soda the melting-point goes still lower. It is also used in making enamels for brick and metals, for false teeth, and inferior qualities are used as bonding materials for abrasive wheels, such as emery, corundum, etc. The addition of alumina to a glass mixture makes opalescent glass; and as feldspar contains it in a readily fusible form, it is used in making opal glass. Very finely ground feldspar is used in preparing certain scouring soaps and polishes.

*Fuller's earth* is a clay showing no specific quality in its chemical analysis, but appears to be a product of the degeneration of feldspar. It has the property of absorbing certain substances, and it is used in chemical industry for clarifying petroleum, lard, cotton-seed, and other oils. Here we touch colloidal chemistry again.

*Mica* is closely related to feldspar in a chemical sense, being a class of minerals consisting of silicates of alumina and an alkali. Physically, however, mica behaves something like asbestos. It is very resistant to electricity and to heat. It may be split into thin sheets, and is used as insulating material in many electrical apparatus as well as for stove windows, furnace peep-holes, and the like. Very finely ground mica that is free from quartz is mixed with heavy grease and used as a lubricant. In order to produce a scintillating surface on wall-paper, white mica is ground very fine under water and then attached to the paper by means of an adhesive. It comes from India.

Boron is related to aluminium in the periodic table, and, like aluminium, it is tri-valent. It goes into com-

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bination very much as aluminium does, but here the cousinship ends. Aluminium is a metal, but boron is not; in a free state (in which it is not found in nature) it is a brown, amorphous powder. It forms an oxide,  $B_2O_3$ , which is the anhydrid of boric acid, also known as boracic acid; the two expressions are names for the same thing. There are several kinds of boric acid, differing only in the number of molecules of water combined with the boric oxide,  $B_2O_3$ , but we shall not consider them in detail. It is a very mild acid.

The best known salt is borax, which is, chemically speaking, sodium tetraborate,  $Na_2B_4O_7 \cdot 10H_2O$ , and this is mildly alkaline, because the sodium pulls harder one way than the boric acid does in the other. In this form boron finds its greatest use—in the glass industry, as a preservative, as a mild antiseptic in ointments and lotions, in soap, as a cleansing agent in laundries, for soldering (to clean metallic surfaces), and for many other purposes.

## XIII

### LIME AND MAGNESIA

Calcium—Lime and Mortar—Uses of Lime—Calcium Salts—Bleaching-powder—Carbide of Calcium—Gypsum—Cement—Magnesium—Uses—Its Virtues and Its Vices—Fixing Nitrogen with It—Why Sea-water May Not be Used in Boilers—Meerschaum—Asbestos—Talc and Soapstone.

CALCIUM is another of the chief constituent parts of the earth, it being fifth in the order of the elements, and constituting about  $3\frac{1}{2}$  per cent. of the crust of the earth. It is found in rocks as limestone, marble, and chalk, and in coral reefs, all of which are in the form of the carbonate, with, of course, impurities added. Dolomite is a double carbonate of magnesium and calcium. Whole ranges of mountains are composed of it. As the phosphate it occurs in the phosphate rocks of Florida, South Carolina, and elsewhere, so valuable for fertilizer. As gypsum or the sulphate, it is also very plentiful, and it is an important base in the greater number of natural silicates. Sea-water contains calcium salts. The bones of fish and of vertebrate animals and the shells of mollusks are chiefly calcium phosphate. Calcium salts are always present in plant tissues, concentrating mainly in the leaves. It enters into many kinds of glass, as we have seen, and, as we shall see, it is a necessary constituent of cement and mortar.

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In a pure state it is a silver-colored white metal, soft enough to be cut with a knife—but not so soft as sodium or potassium—and it may be broken with a blow, which shows the fracture to be crystalline. Gently heated in the air, it burns with incandescence to the oxide of calcium, or quicklime,  $\text{CaO}$ . If metallic calcium is heated to a dull-red heat in a current of nitrogen, it leaves a spongy mass that contains nitrogen in combination. It fixes both nitrogen and oxygen from the air. Here we have a very simple way of getting nitrogen into combination, which is so much wanted and which requires so much power to accomplish or such a heavy outlay for plant to produce ammonia by the Haber process. The only difficulty is to get the calcium out of the abundant limestone. As yet the process is too expensive.

Fluorine attacks calcium violently at ordinary temperatures, but the other halogens do not combine with it until heated up to four hundred degrees. There is a hydride,  $\text{CaH}_2$ , which is a white solid, which decomposes with the liberation of hydrogen in the presence of water.

Lime we know as quicklime, which is the oxide  $\text{CaO}$ , or anhydrous lime, and as slacked lime or calcium hydroxide,  $\text{Ca(OH)}_2$ , or amorphous lime; but the term is loosely applied to calcium products generally, as limestone, the carbonate, and soda-lime glass, the double silicate. Let us first consider the oxide, or quicklime. It is produced by heating calcium carbonate in one form or another, as limestone, marble, chalk, etc., to redness. If the raw material contains clayey matter—that is, aluminium silicate—the product is more of a cement than a lime, and these impurities may do no harm for building operations, which, as we know, is one of the great uses of lime. On the

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other hand, if the raw material contains magnesium, it may cause serious trouble in building, as the magnesia hydrates, or takes up water much more slowly than lime, and this may take place after the mortar is in place. Then the expansion due to the slacking of the magnesia may destroy the mason's work.

Did you get this? I think it a very good example of the cousinship of elements. First let us note that mortar is a mixture of sand and lime. The slacked lime and water form a jelly-like mass which is stiffened by the sand. Then, when the water evaporates, the lime hardens and becomes much stronger. On gradual exposure to the air the carbonic-acid gas ( $\text{CO}_2$ ), which is always present along with moisture, reacts upon the lime or calcium hydroxide and forms carbonate of calcium or a kind of limestone mixed with the sand. (Limestone and marble, you may remember, are both of them carbonate of calcium.) Limestone is better than mortar; it is stiffer and holds better. This is proved by the fact that good mortar becomes stronger with age.

Now, if the lime contains magnesia, the  $\text{MgO}$  (magnesium oxide) acts like lime ( $\text{CaO}$ ), only it is *very* much slower. Long after the lime has been slacked, the mortar made, and the wall built, the  $\text{MgO}$  begins to slack and swell just as the quicklime did when the mason first put water on it. It goes through the same process, several weeks or even longer afterward—and as the wall gives way you proceed to give the mason fatherly advice. Calcium and magnesium do not drive well in double harness; they have such entirely different ideas of speed.

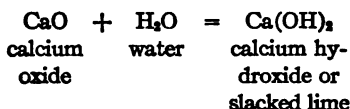
The other great use for quicklime is in chemical manufacture. Indeed, lime, either as quicklime or slacked (as the oxide or the hydroxide), is probably the



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best known of all heavy chemicals. It was known to the ancients, and the art of making it is so simple that it never has died out in all the many centuries of ignorance and weariness of spirit that from time to time have fallen upon humanity. Of course there are refinements in manufacture, and special kilns are designed with occasional saving of fuel; but there is not very much to worry over in the making of lime from limestone except to keep the product dry. The graven marble images of the heathen gods of the Greeks were effectively turned into this raw material for mortar by the pious followers of the Prophet. We can well imagine the gusto with which some lovely head of Pallas Athene was hurled into a kiln—to make the mortar to stop a rat-hole in the hut of a goat-herd of a more orthodox if not a more enlightened day.

The hydroxide of calcium or slacked lime is the product of quicklime and water. The operation is expressed, chemically, as follows:



It takes place with liveliness and the evolution of considerable heat. Owing to this thirst for water, lime is extensively used as a drying agent.

Lime is slightly soluble in water; more so in cold than in hot water, which we may put down as one of its little individualities. Milk of lime is water with more lime in it than will dissolve.

Calcium chloride,  $\text{CaCl}_2$ , is found in the waters of nearly all springs and rivers and in the sea. It seems as though nature were engaged in constantly pro-

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ducing more and more calcium chloride and letting it be carried down to the sea, where, in the course of time, as we have noted before, calcium chloride and sodium sulphate seem to exchange their acids and become sodium chloride, or common salt, and calcium sulphate, or gypsum. Then they stay there.  $\text{CaCl}_2$  is a by-product of a number of chemical processes, especially of the manufacture of soda by the Solvay or ammonia process. It is one of those chemicals that, as noted elsewhere, is still looking for a job, the only general uses being that of keeping roads moist in dusty weather, for making anti-freezing mixtures, and other purposes, none of which demands the amount that is available. It has an intense deliquescent or hygroscopic quality, which means that it has an almost human thirst. One hundred parts of chloride of calcium, exposed to an atmosphere saturated with atmospheric vapor, will absorb 124 parts of water in ninety-six days. One hundred kilos (220 pounds) of Bavarian man, exposed to opportunity, will absorb more than 124 kilos of beer, which is over 90 per cent. water, in less than ninety-six days.

Calcium hypochlorite,  $\text{Ca}(\text{OCl})_2$ , may be prepared, but bleaching-powder, or "chloride of lime," is more interesting. This has enormous uses, and is made by allowing chlorine gas to act upon slacked lime  $\text{Ca}(\text{OH})_2$ . The lime is spread three or four inches deep on perforated shelves in large chambers and the lime raked into furrows. Chlorine is led through the chambers, and the reaction proceeds rapidly at first and then slows down. The lime is occasionally raked over to expose fresh surfaces, and after standing twelve to twenty-four hours a shower of lime dust is blown into the chambers to absorb the excess of chlorine. The result is not calcium hypochlorite,  $\text{Ca}(\text{OCl})_2$ , nor

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is its chloride of calcium,  $\text{CaCl}_2$ . It was supposed to be a molecular compound of both  $\text{CaCl}_2$  and  $\text{Ca}(\text{OCl})_2$ ; but this is not likely, because the chlorine can be expelled from it if carbon dioxide,  $\text{CO}_2$ , is blown through it, and calcium chloride,  $\text{CaCl}_2$ , will not give up its chlorine to  $\text{CO}_2$ . Then calcium chloride is very deliquescent—that is, it absorbs water, and bleaching-powder does not do this to any appreciable extent. It is not calcium hypochlorite, as proved by analysis, but it appears to be chiefly a mixed salt of the formula

$\text{Ca} \begin{array}{c} \diagup \text{OCl} \\ \text{---} \text{Cl} \end{array}$  or  $\text{CaOCl}_2$ . With it is some slacked lime, because it does not take up the theoretical amount of chlorine—and analysis shows this, too.

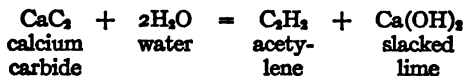
In bleaching fabrics they are steeped in a dilute solution of bleaching-powder, which is not wholly soluble, leaving some lime as a precipitate, and which shows a strong alkaline reaction. Then goods are dipped in a dilute acid solution, and washed. The effect of this alkaline bath and subsequent acid bath upon the cellulose of the fabrics is to disturb it chemically—and oxygen is always at hand. The oxygen, so to speak, sees its chance, and proceeds straightway to oxidize the cellulose to oxycellulose, which is an amorphous powder. Then we say the cloth is rotten, and complain that they do not make good materials any more.

In sanitation, bleaching-powder is one of the most effective agents. It has been claimed that it is more effective than chlorine gas, but modern practice seems to take to free chlorine, when it can be used conveniently, in preference.

Calcium carbide,  $\text{CaC}_2$ , is an important product made by heating lime and coke in an electric furnace. The reaction  $\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$  takes place,

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and the carbide is used to produce acetylene gas for lighting:—



The high temperature of the electric arc is needed to make the calcium carbide. A new development of the carbide industry is the production of calcium cyanamide,  $\text{CaCN}_2$ , or nitrolime, or *Kalkstickstoff*, as the Germans call it, meaning chalk-nitrogen. To produce it, calcium carbide is brought into contact with nitrogen gas, obtained by the distillation of liquid air. They are maintained at a heat of  $800^\circ$  to  $1,000^\circ$  for a time, after which the calcium cyanamide or nitrolime is found as a coke-like material. This is ground to powder and constitutes one of the great new methods of bringing nitrogen into the soil. The art of making synthetic ammonia by treating  $\text{CaCN}_2$  with steam we discussed under the subject of nitrogen.

Calcium phosphide is interesting stuff. It is made by heating lime and red phosphorus and is a reddish brown crystalline body. When thrown into water it instantly decomposes with the evolution of phosphorated hydrogen, which is spontaneously combustible. For this reason it is used to make signal-fires at sea. About one pound is placed in the lower half of a tin can. A hole is jabbed into the bottom and another into the top of the can before it is thrown overboard. The can is supported by a wooden float. Water penetrates the lower hole and the gas issues from the upper outlet, igniting immediately on contact with the air. It burns with a flame from nine to eighteen inches high and lasts about half an hour.

Calcium sulphide,  $\text{CaS}$ , has the peculiar quality,

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after it has been heated, of shining in the dark for a time after exposure to light. It is therefore used in the manufacture of luminous paints. Zinc sulphide has the same property.

Gypsum is calcium sulphate, and so is plaster of Paris,  $\text{CaSO}_4$ . Gypsum occurs in nature, and when a part of the water with which it crystallizes is driven off it is called plaster of Paris. As such it finds its chief uses as a cement, for plastering walls, and for the reproduction of sculpture. The process of setting is still within the realm of theory, and we shall not try to solve it. Natural gypsum of very fine texture and having a translucent quality is called alabaster.

By cement we mean calcareous compounds used in building; not adhesives, as typified by glue. A brick-layer named Aspdin, of Leeds, England, in about 1845, calcined a mixture of chalk (calcium carbonate) and clay (aluminium silicate) and found that the product, when ground and mixed with water, would set. In other words, he took Thames chalk and Medway mud and heated the mixture. It looked like a building-stone known in those regions as Portland stone, and so the name Portland cement arose. While engaged in making his mixture he is said to have attired himself in a long black robe and the pointed cap of the necromancer and to have uttered curious incantations while at work. He had a tray with several compartments, in each of which he had various powders which he would scatter into the kiln as his operations proceeded, and he accompanied this with a grand display of jargon which was supposed to be black magic. He had also a neighbor named Johnson, and Johnson was endowed with more curiosity than belief in magic. He discovered that the magic powders on Aspdin's tray were powdered sulphate of copper, limestone,

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and other ingredients, but the content of the cement baffled him. It also baffled the chemist whom he employed to analyze it, for he came to the conclusion that it was calcium phosphate. So Johnson proceeded to calcine the bones of animals until his neighbors protested against the lively smell. But Johnson continued to experiment until he succeeded, and then the industry really began.

Portland cement is the most important of all cements. It consists of compounds of lime and silica and of lime and alumina. These are necessary, but it commonly contains other compounds of lime, with ferric oxide, magnesia, insoluble silicates, some sulphates, and then some more. The important constituents are lime, silica, and alumina in proper proportions. These bodies exist in the cement in the form of double and treble salts—*viz.*: tricalcium silicate,  $3\text{CaO}.\text{SiO}_2$ ; dicalcium silicate,  $2\text{CaO}.\text{SiO}_2$ ; and tricalcium aluminate,  $3\text{CaO}.\text{Al}_2\text{O}_3$ ; and these do not exist separately, but rather in a solid solution in the Portland-cement clinker. They are not definite compounds, but solid solutions, like glass. Just what happens when cement sets is not very well determined, but what seems probable is that a soluble calcium aluminate is dissolved, and that this straightway deposits an insoluble hydrous or combined-with-water calcium aluminate, which "sets."

So, to make cement, one proceeds to heat in a kiln limestone, marble, chalk, or marl, all of which consist chiefly of aluminium silicate. There is, in some localities, "cement rock," which contains lime and clay materials, but the cement made from this material is usually inferior in quality. The reason is simple: if you grind up natural rock and fire it you have to take what comes, whereas in making so-called

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"Portland cement" the proportion and the purity of raw materials are under constant control, and a much better quality of cement may be obtained.

In the manufacture of Portland cement, the usual proportions are about one part of clay (aluminium silicate) to three parts of calcium carbonate (limestone, etc.), and the materials are thoroughly dried by heating in rotating drums. The mixture is very finely ground and is fed into the upper end of long, rotating cylindrical kilns set on an inclined plane and lined with fire-brick. A very hot flame, usually obtained by burning coal after first bringing it to the condition of a fine powder, is forced in at the lower end. During the passage the reaction takes place, and just before the product reaches the tremendous temperature of its melting-point it is removed from the kiln. It is called cement "clinker," and it is then ground to a fine powder and packed in barrels, etc., with the warning pasted on it, "Keep in a dry place."

Natural cements do not require so much heating as the Portland variety.

Another very good cement is made of blast-furnace slag. The slag, as it flows in a molten mass from the blast-furnace, is granulated by a stream of water directed against it. It dries quickly, and then it is ground to a very fine powder. Dried slacked lime is added to the powder and is ground up with it, and, in accordance with the content of the slag, other correctives are added. Then it is calcined. The trouble-maker is magnesia,  $MgO$ , because, as we noted in treating of lime and mortar, the magnesia is tricky.

Since cement will set without the presence of air, it will set under water about as readily as it will anywhere else.

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Cement is not often used alone, but rather in conjunction with sand, gravel, broken stone or rubble, in the proportion of about one part of cement to four parts of rock material. A good concrete of this sort will stand pressures of five thousand to seven thousand pounds per square inch, without being crushed. Walls built of concrete hold better if reinforced, as the term is, with twisted steel rods, running one way or crossed when the concrete is poured into forms, leaving the rods firmly embedded in the concrete.

Eighty-seven million six hundred and eighty-five thousand barrels of Portland cement were consumed in the United States in 1915. All parts of our country are now well supplied with mills for the manufacture of Portland cement, and the supply of raw materials is practically inexhaustible.

Magnesium is an alkaline metal and is found very wide-spread in nature, usually connected up as a double salt with some other metal. It is not found in a free state because of its avidity for oxygen, with which it combines to form magnesia,  $MgO$ . In time with water this becomes the oxyhydrate  $Mg(OH)_2$ , and again, in more time, the carbonic acid of the air, if it can get at it, will produce the carbonate. Although in a pure state it can be kept exposed because it becomes coated with a thin crust of  $MgO$ , the oxygen will surely get it in time.

It is stable enough with its coating of the oxide, provided it is in large enough pieces. If we cut the light, silvery-white metal (which pure magnesium is) into thin strips, we can light it, and it will burn with an intensely luminous flame to the oxide  $MgO$ . For this reason it is used for fireworks, for shrapnel trailers, to show where the projectiles land, and for illuminating bombs to make daylight over the enemy's works



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and trenches. It is also used in photography for flash-lights.

It is produced by fusing minerals containing it and making a separation by electricity. Improved methods of producing magnesium have been developed in the United States since the foreign supply was shut off by the war. It appears very likely that the development of these processes will result in much cheaper metallic magnesium than we ever have known before. Its uses in metallurgy are increasing very rapidly. Although, as we have observed, slivers of it will burn easily, larger blocks of it will not, and when it is alloyed with other heavier metals this hazard is entirely removed. It alloys remarkably well with aluminium and with other metals in the place of aluminium. It machines easily and well, and it casts beautifully. It is one-third lighter than aluminium and over twice as strong, so that the prospect of reducing the weight of high-speed engines for air work, etc., and at the same time increasing their strength, is very favorable. Steel-makers find it valuable for "scavenging," because a little magnesium thrown in when the ingots are cast will combine with the air that may be bubbling through and likely to weaken the center of the ingot by not getting out fast enough. That it will combine with the oxygen is easy enough to understand, but it does more than that. Magnesium combines with nitrogen direct to magnesium nitride,  $Mg_3N_2$ , at white heat. Here would be another way to fix atmospheric nitrogen except for the cost of magnesium.

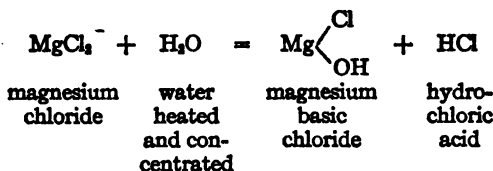
We have considered it as a useful metal. As the oxide, magnesia,  $MgO$ , it is useful, too, but also one of the worst of nuisances. We have already referred to it in this connection under the subject of lime, with which it is so often associated.

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On the other hand, magnesia is coming into frequent use in building operations for making fire-proof flooring, where the process is kept under chemical control. Various salts of magnesium are also used for this purpose.

The chloride  $\text{MgCl}_2$  is important. In the Solvay soda process, as you may recall, magnesia may be used instead of lime to drive the ammonia from the ammonium chloride. The reaction is the same, except that we have as a waste product magnesium chloride instead of calcium chloride. But magnesium chloride is not very stable, and heat will drive the chlorine out of combination with the magnesium. So, on heating it, the chlorine is freed and saved, while the magnesium oxidizes at that temperature to magnesia,  $\text{MgO}$ , and is used over and over again on the ammonium chloride. And by this method nothing is lost.

This instability of magnesium chloride is the reason why sea-water may not be used in the boilers of steamships. Sea-water contains it in considerable quantity. The heat drives out the chlorine, which takes on hydrogen from the water and becomes hydrochloric acid, and with free muriatic acid in the boilers we do not have to explain what would happen. Here is the reaction that takes place:



Magnesium chloride is very deliquescent—that is to say, it is hygroscopic, which means that it is ex-

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ceedingly thirsty for water. It is magnesium chloride,  $\text{MgCl}_2$ , in common salt as an impurity that makes it take on water as it does.

Magnesium is found in soils, and the German Potash Syndicate, which sells a fertilizer of mixed potash and magnesium chlorides, advertises that the magnesium is of material value in discouraging the development of cut-worms and other noxious organisms that destroy plants. We live and learn.

Serpentine and meerschaum are hydrated disilicates of magnesium. Asbestos is an anhydrous silicate, and is found in large deposits in Canada. It is a rock crystallized in long, fine fibers of a silky appearance which may be easily separated, spun into yarn and rope and woven into cloth. Asbestos is not affected by heat save on very long exposures; it is in effect non-combustible, and it is not attacked by common acids. It is widely used for insulation and fire-resisting purposes.

Talc and soapstone are acid meta-silicates of magnesium, or  $\text{H}_2\text{O}$ ,  $3\text{MgO}$ ,  $4\text{SiO}$ . Finely powdered talc is used for toilet-powder, as a filler and coating for paper, for cloth window-shades, as filler for cheap toilet soaps, and many other purposes. Soapstone is used for griddles, stone linings, switchboards, laboratory table-tops, furnace linings and acid tanks.

The mixtures of calcium and magnesium in minerals is so persistent, especially as carbonates, that we may as well review a few of them.

Calcite or calc spar is calcium carbonate, and is common in veins as well as being one of the most widespread rock-forming minerals.

Magnesite is magnesium carbonate, and occurs generally as a decomposition product of magnesian rocks.

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Dolomite is a mixture of calcite and magnesite.

Limestone is a sedimentary rock, and when pure it consists of calcium carbonate. When it is crystalline it is called crystalline limestone, and if the texture is fine it is called marble.

Chalk is a soft, powdery white variety of limestone. Finely ground chalk from which the impurities have been removed is called whiting, or Paris white.

Calcareous marl is clay mixed with calcium carbonate.

## XIV

### IRON AND STEEL

Chemical Habits of Iron—Metallurgy—What Happens in the Blast-Furnace—James Gayley's Invention—Furnace Gases—Wrought Iron—How Steel Is Made—Bessemer, Open Hearth, Crucible, and Electric Processes—Tempering—Special Steels—Combinations of Iron—Ores—The Future.

ABOUT 5 per cent. of the crust of the earth is iron, and it is everywhere. It is not found in a pure state because in time the oxygen will get it—whether it watches out or not. No kind of paint or covering is absolutely stable, and when it cracks there come the oxygen and some water from somewhere, some time, and the iron turns into rust, which is ore. All the iron and steel now manufactured by the millions of tons is, cosmically considered, in a transient state. It is bound to go back into combination in time, and most of it as ferric oxide,  $\text{Fe}_2\text{O}_3$ . Only in one place in nature do we find it in quantity free and uncombined, and that is in meteorites; which are dropped down upon the earth out of the empyrean. So there is no oxygen up there in the blue between the stars.

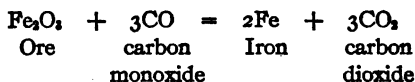
Iron has two methods of combining—with three hooks, called ferric compounds, and with two hooks, called ferrous compounds. It occurs most freely as the oxides,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ , and as the carbonate,  $\text{FeCO}_3$ .

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These are the favorite ores. It is also found as pyrites or the sulphide,  $\text{FeS}_2$ , which is roasted to get out the sulphur for sulphuric-acid works, after which the remaining iron with its impurities is available ore for blast-furnaces. It is also found in silicious rocks, in the earth, in many plants, and dissolved in water. We also have a little of it in our own make-up.

Of course magnetite, or magnetic ore, is not pure  $\text{Fe}_3\text{O}_4$ , and neither is any other ore pure. If there is enough of the oxides or carbonate or other ferric or ferrous (iron in combination with three hooks or two) compounds the ores are workable. Too much silicate makes it hard to manage.

Theoretically the metallurgy of iron is very simple, but in practice it is not simple at all. The problem is to bring the iron out of the ore. So coal, usually in the convenient form of coke, and iron ore and limestone are brought together in the fiery furnace, and air is blown in so that a very high temperature is produced. The coal is burned to carbon monoxide,  $\text{CO}$ , and this combines with the oxide of iron in the ore to produce carbon dioxide,  $\text{CO}_2$ , and sets the iron free. Let us write out the equation:



The iron, being the heaviest of all the things put into the furnace, sinks to the bottom in a molten state. But a great many things have been happening in the mean time. The iron ore, coke, and limestone are fed in separate layers. Then air, which is blown in from below to feed the fire, partly burns the coke to producer gas,  $\text{CO}$ , and this, combining to  $\text{CO}_2$ , causes heat enough

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to melt up and generally decompose the compounds in the furnace. The carbonic acid,  $\text{CO}_2$ , is driven from the limestone and escapes. The calcium from the limestone combines to make double salts with the silicates which are sure to be in the ore, and this is a sort of glass. So now we have at the bottom of this long, upright, somewhat egg-shaped blast-furnace (with the big end at the bottom) the molten iron in a cylindrical extension underneath the big egg. Above this is the slag, or molten, glassy silicates of lime with other things in suspension or dissolved in it, and over that are the layers of the furnace charge, slowly moving down. The bosh, or that part of the furnace where the sides contract suddenly, provides that the pressure upon the slag is not very great. In effect, the pressure is only that of a cone of the charge immediately above it. Air comes through from the bottom upward, like real blazes. The heat of the molten iron is too great for oxygen to combine with it, and it is protected from oxidation from above by the covering of the molten, glassy slag.

At regular intervals the blast is stopped and the furnace is tapped to let off the slag in one direction, and from another tap, lower down, the iron is run off into molds. When it cools and is taken from the molds it is pig-iron. The slag formerly had no value except to fill in hollow places, as rock, but now it is used to make Portland cement, because of its content of the silicates of aluminium and calcium. For reasons explained elsewhere, no magnesium is wanted in the slag that is used for cement. As soon as the iron and slag are run off the blast goes on again, and the feeding of coke and ore and limestone also continues.

The air always contains moisture, and, as we have

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observed under "Hydrogen," the warmer the weather is the more moisture the air can hold in suspension. For many years it was observed that blast-furnaces behaved better in winter than in summer. So Mr. James Gayley, a well-known American engineer, conceived the idea of refrigerating the air before it was blown into the furnace, to get out the moisture. He was known as a competent engineer and a man of ideas, but the wiseacres shook their heads. "Too bad about poor Jim Gayley," they said. "He's ——," and they tapped their foreheads and shook their countenances some more. "He thinks he can heat a blast-furnace with an ice-machine," was a characteristic comment. And their wives felt very sorry for Mrs. Gayley, and wondered if they had not better call and see if they could help—and find out something.

The Gayley process of refrigerating air before use in blast-furnaces saves from one to two dollars a ton in the cost of pig-iron. And Mr. Gayley is a very prosperous man. Some day, maybe, somebody will discover a cheap way to separate water into its oxygen and hydrogen. It doesn't seem likely, but it may come. Then the burning hydrogen would save a great deal of coal and the oxygen would be there to burn it with. Or a very cheap method of liquefying air may come to our ken. Then, with the nitrogen distilled off, there would be only one-fifth as much air to heat. And yet this might not save so much, because that heated nitrogen that goes into the furnace and then comes out again does a lot of good work. It helps to dry out and pre-heat the ore and coke and limestone before the reaction begins. The gases escaping at the top of the furnace are not very hot.

Mr. J. E. Johnston, a well-known authority on blast-furnace practice, has computed the results of



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using a blast of 50 per cent. oxygen, and has designed a furnace to meet the situation if some invention should provide us with 50 per cent. oxygen at a low cost. It looks, after all, as though a considerable saving in coal would be effected by it.

Furnace gases are now studied, and they prove an interesting subject. They have sufficient heating value to drive the gas-engines to blow the blasts—and then some more. They contain pieces of coke, which are saved. They have to be washed before they are led into the gas-engines to get out the sulphur fumes, which would play hob with the cylinders. They contain also particles of potash, as sulphide, cyanide, and in other forms in suspension. The Research Corporation is working on the problem of conserving this potash, with a view to bringing it down by electric precipitation. A very interesting suggestion has lately come from Doctor Cottrell which will be tried out shortly. It consists in adding high potash feldspar to the furnace charge. This should produce a better iron by making it more free from sulphur, which the potash should carry off in the gases as potassium sulphide. And the potash might then be brought out of the gases by washing and electric precipitation. We referred to this in the introduction.

Now pig-iron is iron all right, but we must remember that it is also a great deal more. We have had it in a liquid state, and as a liquid it dissolved some things that will and some that will not stay in solution in the cold. Pig-iron carries a high percentage of carbon—from 3 to 5 per cent. Some of this is combined with the iron as iron carbide,  $\text{Fe}_3\text{C}$ , but a large part of it is scattered through the metal as graphite, in flakes. Graphite, as we shall learn when we come to carbon, is an allotropic form of that element and is just the

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thing not to have in iron. It keeps the particles apart, makes the iron brittle, and it does not do any good at all. Then there are other impurities present, such as sulphur, phosphorus, and silicon. Silicon has its uses when it is needed, but sulphur and phosphorus are rarely of any use to it, and each of them is generally an infernal nuisance—in iron.

When pig-iron is melted up and cast into molds, it is cast-iron. Of course the foundryman should know what he is putting into his cupola, so that he may know also how his product will behave after it comes into use. Any old pig-iron, or "No. 2 Foundry," will not take care of the foundryman's problems to-day.

Steel differs from cast-iron in two particulars: it contains less than 2 per cent. of carbon, and what carbon there is in it is combined with iron as iron carbide,  $\text{Fe}_3\text{C}$ . There is no graphite in steel. Generally speaking, the higher the carbon content the harder the steel. But there are refinements in the form in which the carbon exists in the steel which we shall discuss when we come to tempering.

Wrought-iron is also free from graphite and its carbon content is low, as low as a low carbon steel—from  $\frac{1}{2}$  to  $\frac{1}{8}$  per cent. The method of manufacture leaves a slight proportion of slag, from  $\frac{1}{10}$  to 2 per cent. This slag takes the form of long threads extending through the iron and thus gives to wrought-iron a fibrous structure not known to steel. To make wrought-iron, pig-iron and ore are heated in a reverberatory furnace, and the puddlers work it with rods until the impurities are melted or driven out. The more it is wrought (or worked or hammered or rolled or pounded) the tougher it becomes.

To make steel, boil iron, and there are several ways

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of doing it. The Bessemer process is the cheapest, and the worst. The molten iron is run from the blast-furnace into a ladle instead of into molds, and is poured into a cylindrical vessel with a funnel-shaped top, which tips on its axis. This is called a converter. Air is blown through from the bottom. This blows out the graphite, it oxidizes and blows out the sulphur and other impurities, the remaining carbon is converted into carbon dioxide, and we have a much purer iron. At this point a special iron rich in carbon, manganese, and silicon is thrown in. The carbon provides that which is needed in the steel, the manganese prevents the formation of iron oxides, because, all things being equal, oxygen likes manganese better than iron, and the silicon is said to prevent the formation of bubbles or blow-holes in the ingots, although it makes the steel more brittle. And still they suffer from blow-holes. Then the converter is tipped on its axis and the contents run into great molds. These are ingots. Other metals, such as magnesium, etc., are sometimes added before the ingots are cast, with a view to taking up oxygen and boiling away with it.

The Bessemer process is a very rapid one; over twenty tons of steel may be converted in half an hour from pig-iron in a single converter. The operation is regulated according to the color of the flame, and it is beautiful to watch. If we had only more esthetic sense and understanding, Bessemer steel-mills would be great show-places.

One trouble with the process as designed by Sir Henry Bessemer was that with the fire-brick lining the phosphorus was not driven out. Fire-brick being chiefly a silicate of lime, a lining made of them is called "acid," because of the  $\text{SiO}_2$  in them. So Bessemer converters with an "acid" lining are good only

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for converting high-grade iron, with a very low phosphorus content. Bessemer ore, so called, is that which carries very little phosphorus. An improvement over the acid lining has been devised by substituting magnesium and calcium oxides for fire-brick. With this, for obvious reasons, so-called basic lining, the phosphorus may be more completely eliminated and lower grades of iron may be used.

But the Bessemer process does not make a pure, reliable quality of steel. It is used for rails and some structural shapes and steel castings, but what with the quick work, the high temperatures not under good control, and the general slap-dash of the process the product is not always dependable.

The open-hearth process was designed by Sir William Siemens, and it takes nearly as many hours to convert a large charge of iron to steel as the Bessemer process takes minutes to convert a small one, but it makes better steel. The charge is pig-iron, iron oxide (ore), limestone, and scrap iron and steel. It is heated by a mixed blast of air, and gas is blown over the saucer-shaped furnace. The slag is separated and the steel cast into ingots. The tendency is to increase the size of open-hearth furnaces; some installations with a capacity of two hundred tons each are in successful operation.

Later practice shows economy in combining the processes. The iron is first treated in a Bessemer converter, and then, but for a much shorter time, in large open-hearth furnaces. The product is open-hearth steel.

The good old prehistoric way, the method employed by the Saracens to make Damascus blades to destroy the unbelievers; the sword of the Chinese executioner who cut off the heads of his victims with

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such skill that they did not know anything had happened until he graciously gave them a pinch of snuff, and, by the jerk of the sneeze which followed, they discovered themselves to be headless; the sword of Siegfried and the marvelous Excalibur—all these must have been made by the crucible process. By this method the best steels and those of special contents are made, although it is being superseded in many places by the electric furnace. The crucibles or pots are made of graphite and hold about a hundred pounds of iron. To make the best quality, wrought-iron bars are melted up with the necessary amount of carbon in the form of coke, because the graphite of the pots will not combine to produce iron carbide. Often the charge is open-hearth or Bessemer steel. Some limestone is added to make a flux for the impurities, and then whatever is needed is added to make the steel just what the buyer wants. The operation is under constant control, but of course it is expensive. Nevertheless, makers of machinery are beginning to demand the very quality of steel for each part of their machines that will best serve its purpose and last longest. The discovery of special steel alloys for special purposes is, as we have said before, becoming one of the sportiest features of applied chemistry, and many of them are made in crucibles. Some special steels are made in open-hearth furnaces, and still more in electric furnaces.

The electric furnace is a late development, whereby Bessemer or open-hearth steel may be quickly refined to very high grades. The steel is poured into the furnace in a molten state and two carbon (graphite) electrodes are dipped into it. The passage of the current through the molten iron produces great heat, and the impurities and nearly all the carbon are

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driven off. Carbon is reintroduced, together with whatever else is needed to make the steel desired, and the whole operation, with furnaces containing twenty tons and more, is completed within two hours.

Electric converters are supplanting crucibles in considerable measure. According to a recent statement of the chief engineer of one of the largest automobile companies—and these are great consumers of special steels—it was declared that they prefer steels made in electric furnaces to those made in crucibles. The electric converter is in effect a different way of doing the same thing that is done in crucibles, but on a much larger scale. The best practice of to-day seems to point to steel made in two consecutive stages direct from the blast-furnace without cooling—first in Bessemer and then in electric converters. This provides for economy and quality at the same time.

Tempering.—If we heat a high carbon steel to a high temperature, the very hard iron carbide will dissolve in the iron, and we have a solution of iron carbide in iron. Now if we cool it suddenly the carbide will not have a chance to crystallize out, and we have a cold solid solution of iron carbide in iron. This is a very hard steel, but it is too brittle for most purposes. So let us heat it again, but not to so high a temperature as before. Some of the iron carbide will come out of solution and will stay there, leaving the mass as iron with carbide in solution mixed with some carbide which is not dissolved in it. The steel is then not so hard, but it is less brittle. This is tempered steel, tempered according to the quality we want it to have. Tempering, of course, treats the steel after it is made, and tempering will not make good steel out of poor material.

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We have spoken of the many kinds of steel that may be produced by making alloys of it with different metals; we shall mention only a few of them:

Nickel steel contains 3 to  $3\frac{1}{2}$  per cent. of nickel. It is very hard, very elastic, and remarkably ductile. It is used for armor plate, bridge cables, propeller-shafts, etc.

Chrome steel, with 2 per cent. chromium, or mixed with nickel as chrome-nickel steel, is hard and elastic when suddenly cooled. It is used for projectiles, for parts of automobiles (as are many other special steels), in rock-crushing machinery, and in safes.

Manganese steel contains as high as 12 per cent. manganese and  $1\frac{1}{2}$  per cent. carbon. This is very hard, no matter what treatment it receives. It is so hard that it has to be cut with emery-wheels; tools break on it. If cooled suddenly it becomes ductile, and if cooled slowly it becomes brittle—the very opposite of high carbon steel.

Tungsten steel runs from 5 to 10 per cent. tungsten, is very hard at high temperatures, and is called “high-speed” steel. This is because metal-cutting tools made of it may be run at a high rate of speed, sometimes so fast as to make the cutting edge red-hot, and yet the steel does not lose its temper. For the same reason it is also sometimes called “self-tempering” steel.

Vanadium steel combines elasticity with great tensile strength.

Copper steel is a late discovery. A small amount of copper, about  $\frac{1}{4}$  of 1 per cent., in the steel will keep it from rusting for a considerable time. While steel alloyed with a small amount of copper does not become rust-proof, the copper acts as a rust retardant to a remarkable degree. Some authorities deny this

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with considerable vigor, but it seems to work, nevertheless.

The manufacture of steel is the greatest of American industries, and when we consider the subsidiary industries built up around and about it, it seems to spread over everything. At the time of the present writing the United States is producing steel at the rate of 40,000,000 tons per year.

When iron is exposed to moist air it becomes covered with a loose coating of rust which is approximately  $2\text{Fe}_2\text{O}_3 \cdot \text{Fe}(\text{OH})_3$ . In dry air the reaction does not take place. Owing to the double life that iron might be said to lead, being bi-valent at one time and tri-valent at another time, there are whole series of ferrous and ferric compounds. The oxides, in a more or less impure state as they are found in nature, are known also by their mineral names. Thus magnetite, which is strongly magnetic, is  $\text{Fe}_3\text{O}_4$ . It is hard, black, and of metallic luster.

Hematite is ferric oxide,  $\text{Fe}_2\text{O}_3$ , and varies in color from red to black in nature, but when finely ground it is usually red. This is Venetian red.

Limonite is a hydrated ferric oxide,  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . It is also known as brown hematite.

Ocher is limonite mixed with clay, and if it contains an appreciable quantity of manganese it is brown and called umber. These oxides, in a more or less pure form, are very largely used in the paint industry, especially hematite and ocher.

There are ferrous and ferric chlorides, and other salts which we shall not mention in detail, except the ferrous sulphate,  $\text{FeSO}_4$ , which crystallizes with seven molecules of water and is known as green vitriol,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .



## IRON AND STEEL

The iron and steel industry touches us more closely than any other, and as wood grows scarcer steel is taking its place. Where steel is not available we often use Portland cement, which is sometimes a by-product of iron, since it may be made from many slags.

Occasionally the question is raised how long the present supplies of ore will last. I have even heard fears expressed that civilization itself is threatened with the exhaustion of iron ores. When we consider that one of the principal uses of steel from 1914 up to the present writing in 1917 has been to destroy life and property in war, it makes us almost doubt the civilizing influence of the great metal. We need not fear, however, that it will disappear. There are vast supplies of iron constantly being discovered, and constant advances are being made in the art of concentrating ores so that they may be smelted economically. By means of modern concentration processes it is estimated that certain deposits in New York and New Jersey alone would furnish 50,000 tons of 60 per cent. ore per day for 100 years and still not be exhausted. Then, too, Tennessee and other Southern States have enormous stores of usable ore. And when the time comes for iron to be scarce, if it ever does, it is a fair guess that aluminium will be obtained direct from clay, and of this the supply is as nearly inexhaustible as anything on earth.

## XV

### MORE METALS

Copper, Zinc, Lead, and Tin—Copper Ores—Flotation—Smelting and Refining—The Righteous Wrath of Neighboring Farmers—Copper Compounds—Alloys—Zinc and Its Ways—Zinc Ores—Production and Use—Galvanized Iron and Brass—Oxides and Salts—Tin and Its Tricks—Production and Use—Lead—Chemical Nature and Sources—Compounds—Production and Use—The Storage Battery—White Lead

**O**XYGEN is certainly a royal and imperial personage among the elements. It claims nearly everything and gets as much as it can. An example of this is the geological position of copper. There are several oxides known, of which the most important are cuprous oxide,  $\text{Cu}_2\text{O}$ , which occurs in nature as cuprite or red copper ore, and cupric oxide,  $\text{CuO}$ , known in its native impure state as melaconite or black copper. But, as greater depth is reached, down below the old water level, the ore has probably remained hidden from oxygen and we are more likely to get the sulphides. It is a salmon-red metal, which is malleable, is a good conductor of heat and electricity, and has considerable tensile strength, so copper utensils may be made with thinner walls than those of iron. The mineral acids dissolve it easily, while the weaker organic acids have little corrosive action, and that is why cooking utensils are occasionally made of it.

Ammonia dissolves it, and, just to show the per-

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versity of nitrogen in all its ways, instead of behaving as a base, as it usually does, it behaves as an acid. This seems to be the body formed, which is called cuprammonium, and is not known out of solution:  $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$ . It is a safe rule never to bet on what ammonia will do in a given situation—unless you happen to know. Analogy is a will-o'-the-wisp in reasoning with ammonia. On the other hand, there doesn't seem to be any nitride of copper—a combination of nitrogen with copper and nothing else, as there is a nitride of magnesium.

The process of mining, smelting, and refining of copper is an enormous industry, and we shall take only a short glance at it. Most of the copper ore smelted is in the form of sulphides, and there are always other metals present with it; but in many lean ores smelting is preceded by concentrating in one way or another, and of these the process of flotation is so interesting that we shall have to describe it.

It consists in grinding the ore to a powder and then feeding it into a tank containing water and a slight amount of oil. As bubbles are caused to rise in the water, by splashing it with ladles or feeding in compressed air, the metal-bearing particles attach themselves to the bubbles and float to the top, while the lighter gangue of limestone or other rock falls to the bottom. The phenomenon is regarded as due to the fact that the oil wets the metallic surfaces and also the surfaces of the bubbles, which carry the oil and the metal to the top. The particles of rock, on the contrary, not being wetted by the oil, do not attach themselves to the bubbles and so fall to the bottom. By this means a 20 per cent. concentrate may be obtained from a 2 or 3 per cent. ore. The process has come into very wide-spread use.

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By burning out the sulphur the smelter owners were formerly in sore straits because the sulphurous fumes,  $\text{SO}_2$ , did not provide for the enjoyment of this life, or even a pleasant intimation of the future in their respective neighborhoods. Farmers lost their crops, their cattle, their tempers, and their milk of human kindness if they chanced to be neighbors. The situation was remedied, as we have explained on another page, by Doctor Cottrell's process of the electrical precipitation of suspended particles, and permitting the sulphurous gas to escape hot through the high stacks and thus diffuse itself and blow away.

There are two methods of smelting copper ores in vogue: in blast-furnaces, which are upright and constructed a little, but not very much, like small iron blast-furnaces; the second method, in reverberatory furnaces, accomplishes the same thing in horizontal structures in which the fuel is burned in a separate compartment from the ore, whereas in a blast-furnace they are mixed. The task accomplished is the separation of the ore into what is known as copper matte and slag. Now matte is cuprous sulphide,  $\text{Cu}_2\text{S}$ , and iron sulphide,  $\text{FeS}$ , in varying proportions, and the next step is to convert the matte into crude copper, which is accomplished usually by melting it and blowing air through it somewhat as in a Bessemer steel converter. Indeed, the process is called Bessemerizing, and the apparatus is known as a converter. Copper and some iron are left, and the sulphurous fumes escape again, only to be disposed of or to make trouble. Then we have a crude, impure copper, which needs to be refined. It is cast into plates and these are suspended as electric poles in a bath of copper sulphate ( $\text{CuSO}_4$ ) and sulphuric acid. Very thin sheets of pure copper form the opposite poles, and the cur-

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rents of electricity are started through. What happens is that the sheets of pure copper are electroplated with the copper that comes from the sheets of crude copper until the crude sheets are eaten away and all of their copper has left its estate of impurity and gone over to abide in a state of grace on the opposite poles.

The impurities, of which there are many, go partly into the solution and fall partly as slime at the bottom of the apparatus. Arsenic and antimony, both of which are likely to be present, do both. Bismuth is precipitated out as its basic salt. Gold, silver, platinum, selenium, and tellurium are not dissolved by the solution and drop to the bottom of the tanks as a mud or slime, from which they are partially recovered. Nickel and cobalt pass into solution and are not plated out so long as there is dissolved copper present.

There are many salts of copper, and they are widely used. Copper chloride,  $\text{CuCl}_2$ , is one of those thirsty chlorine salts. If it is dried *in vacuo* it is pale blue. If crystallized out of a solution it takes with it two molecules of water ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) and forms beautiful grass-green needles. It is a powerful disinfectant, and is also used in calico printing as well as in chemical processes. This is more properly known as cupric chloride; the cuprous chloride, in which copper is monovalent,  $\text{CuCl}$ , is also known.

Copper sulphate,  $\text{CuSO}_4$ , is a white powder, but crystallized with five molecules of water ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) it is known as blue vitriol and has many uses, as, for instance, in calico printing and dyeing. It is used to prevent rot in timber. Farmers soak seeds for some hours in a weak solution twenty-four hours before sowing, to prevent smut. It is applied to grape-vines

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in 10 to 20 per cent. solutions to kill fungous growths. Large quantities are used, although but very little is needed at a time, to kill algæ and other vegetable growth and scum in lakes and ponds.

Copper silicide is made by fusing copper and silicon in an electric furnace at a very high temperature. It is called cuprosilicon, and is silvery white, with a metallic luster, and is hard and brittle. It is used for hardening copper and to add to tin, zinc, and aluminium bronzes to increase their tensile strength and hardness.

The carbonate has never been prepared in a pure state, but compound bodies, such as malachite, which is copper carbonate and copper hydroxide, crystallized together  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ , and azurite, which is  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ , are found in nature. These minerals, when ground, form fine but expensive green paints.

### ALLOYS OF COPPER

Brass contains 18 to 40 per cent. of zinc and melts at a lower temperature than does copper. Its great merit is its resistance to oxygen and its good mechanical qualities. A variety made with but little zinc may be beaten into very thin sheets, and is called Dutch metal. Bronze contains 3 to 8 per cent. of tin, 11 or more per cent. of zinc, and some lead, the rest being copper. Until iron and steel were brought into use, bronze was the metal used for weapons, tools, and castings. For works of art it is highly prized because of its fusibility, its color, and the beautiful patina which covers it, due to surface corrosion.

Gun-metal contains 10 per cent. and bell-metal 25 per cent. of tin.

German silver contains 19 to 44 per cent. of zinc

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and 6 to 22 per cent. of nickel. Aluminium bronze contains 5 to 10 per cent. of aluminium, and looks like gold in color. Silicon bronze contains about 5 per cent. of silicon. It has less conductivity than pure copper, but is twice as tenacious, and is used for overhead electric wires. Phosphor bronze is about 90 per cent. copper, 9 per cent. tin, and 1 per cent. or less of phosphorus. Manganese bronze, for ships' propellers, contains 30 per cent. of manganese.

ZINC is always bivalent—that is, it has two bonds for combining. It is a bluish white metal, used very widely. It is a part of brass, in which it serves the purpose of stiffening and hardening the copper and tin with which it is alloyed. Chemically, it will be electropositive or electronegative, according to the company it is in. If the company is very negative, more so than the zinc, it will be positive, and *vice versa*. Most of its compounds are what we should expect of it as a metal, such as sulphate of zinc ( $\text{ZnSO}_4$ ), chloride of zinc ( $\text{ZnCl}_2$ ), etc.; but along with a very positive radical it will turn negative, its oxide will act as an acid and produce zincates, like zincate of sodium and a few others.

It changes its nature according to the temperature—according to the weather, we might say. Pure zinc, cold, is brittle. At  $120^\circ$ – $150^\circ$  centigrade it may be rolled into thin sheets between heated rollers, and it will then retain its pliability when it becomes cold. At  $200^\circ$ – $300^\circ$  centigrade it becomes brittle again, and at  $418^\circ$  centigrade it melts. At  $916^\circ$  centigrade it boils.

It is reasonably permanent in the air because there is formed a layer of zinc oxide upon the surface, which covers it. Mineral acids attack zinc, liberating hydro-

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gen except when the metal is pure. Then the reaction does not proceed, because little bubbles of hydrogen cover the surface of the zinc and protect it from the surrounding acid. If the zinc is impure, or if a platinum wire or a less positive metal is brought into contact with it in the fluid, the bubbles of hydrogen leave the zinc, touch the other body, and fly away into the air.

It occurs in nature as the sulphide known as zinc-blende, as the silicate, and as franklinite, which is a composite mineral compound of zinc, iron, and manganese oxides. The predominant mineral is the sulphide, and it is one of the leading raw materials in the production of sulphuric acid. The sulphur-free ore is then heated in retorts, producing first a dust composed of zinc and zinc oxide, and finally molten zinc. This is called spelter, and contains lead, arsenic, cadmium, and iron, because these metals are always present in zinc-blende. Electrolytic refining of zinc has lately been introduced. Over 1,000,000 tons of spelter, or crude zinc, are consumed in the world annually, and of this amount about 300,000 tons constitute the American consumption.

Aside from its use in brass, it is used as sheets, often in preference to lead, for roofs, gutters, and architectural ornaments. Cleaned sheets of steel dipped in molten zinc become covered with it, "galvanized," as the expression is, and this protects the iron from rust in two ways: it provides an air-tight covering for a while, and even when the zinc is weathered down it seems to rust in place of iron—that is, the iron does not rust until all the zinc is oxidized. This is different from copper, which encourages corrosion if in contact with iron or zinc, and yet, as we observed under iron,  $\frac{1}{4}$  of 1 per cent. of copper

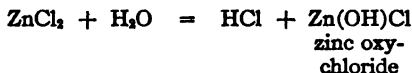


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alloyed with steel seems to decrease corrosion 300 to 400 per cent. Please excuse me for not explaining this. Brass, which is composed of metals of opposite electrical properties, seems to be nearly electrically neutral toward iron, unless it is a red brass, in which copper predominates.

Zinc oxide,  $\text{ZnO}$ , is very widely used as a paint, sometimes mixed with white lead and often in substitution of it. It does not chalk off as lead does, and, on the other hand, it has not the full body. It is called zinc-white or Chinese-white. Artists use it in connection with vermilion, because that is a sulphide of mercury, and if brought into contact with white lead, the sulphur prefers it to the mercury, and so sulphide of lead is formed, which is a dirty black smudge instead of the beautiful red. This is why many beautiful paintings have gone off in quality and lost all their reds, which were made of sulphide of mercury mixed with white lead. Now the sulphide of zinc is white, and if any of it is formed, which is not likely, from contact with mercury, the red may become a little lighter, but that is all. But the preference is usually for white lead if other colors will stand it, because of its greater body. A producer of zinc-white, however, may deny this with vigor, and call you hard names if you say so.

Zinc chloride,  $\text{ZnCl}_2$ , is used as a caustic, as in the presence of water it liberates hydrochloric acid:



Solutions of it are used to impregnate wood, especially railway ties, to prevent the growth of organisms which cause decay. It is also used to dissolve the

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oxides (rust) from surfaces which are to be soldered. The equation given above shows how hydrochloric acid is liberated, which does the work. Like all salts of zinc, the chloride is astringent and poisonous. "Barnett's Disinfecting Fluid," so called, is a solution of zinc chloride.

Zinc sulphate,  $\text{ZnSO}_4$ , is a white salt, known also as white vitriol. It is used in industry and in medicine for external applications. A  $\frac{1}{8}$  per cent. solution is used in certain eye affections.

TIN.—If the elements had consciousness, tin would need a group of eminent counsel to defend it from charges of irregularity. It has two methods of combining—with two bonds and with four. As tin, tinnic, and tinnous compounds did not sound just right to the chemical authors, or possibly they did not know whether to spell the adjectives with one "n" or two, they took the Latin word *stannum* and made their adjectives of that. Stannous compounds are of tin with two bonds, while stannic compounds indicate that four bonds are engaged.

Tin is addicted to allotropy in the worst way. It is a silver-white, crystalline metal of low tenacity but great malleability under ordinary conditions. It also retains its luster on exposure to the air. It is soft enough to be cut with a knife but harder than lead, while not so hard as zinc. Despite its great ductility, which is greatest at about  $100^\circ$  centigrade (the boiling-point of water), it grows brittle enough to be pulverized when it has been heated up to  $200^\circ$ . If a bar of tin is bent, it emits a low, crackling noise, called the "tin cry," said to be due to the rubbing of the crystal faces, one upon the other. It has a great disposition to crystallize on solidification into

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two different forms of crystals according to conditions, tetragonal and rhombic.

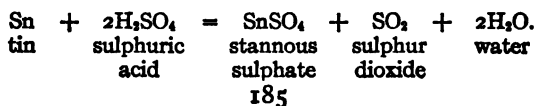
Now if this same tin is cooled to a low temperature it will crumble to a gray powder. This takes place very slowly at ordinary cold-weather temperature, but is likely to proceed very rapidly at  $-48^{\circ}$  centigrade. At temperatures lower than this the crumbling slows down. Organ pipes and roofs have been observed to go to pieces from this "tin pest," or "tin disease," as it is called. If a piece of tin in process of change from its metallic state to the gray-powder form is brought into contact with ordinary white tin, the "disease" will catch. And all the while it is neither more nor less than tin. These forms are merely its allotropic modifications.

It is found in Cornwall, England, in the Malay Archipelago, in Bolivia, Australia, Bohemia, and Saxony. The usual ore is tinstone or cassiterite, and is stannic oxide,  $\text{SnO}_2$ , combined with the arsenical, copper, and other mineral sulphides and tungstates. There is also a comparatively rare tin pyrites, being sulphide of tin, copper, iron, and sometimes zinc. The ore is smelted, and the resultant metal is about  $99\frac{1}{2}$  per cent. pure.

It dissolves in hydrochloric acid to stannous chloride



Cold sulphuric acid attacks it but slightly, while concentrated hot sulphuric acid not only dissolves it, forming stannous sulphate, but it liberates sulphur dioxide:

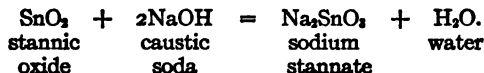


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It would appear to make the sulphuric acid a little nervous by the way it liberates sulphur dioxide.

Pure nitric acid is practically without action on the metal. With dilute, cold nitric acid stannous nitrate is formed; but if brought together with somewhat stronger nitric acid, it oxidizes to metastannic acid—which we shall consider shortly. Observe, please, we have been getting stannous compounds with  $\text{Sn}^{\text{II}}$ , or with two hooks, rather than the stannic with  $\text{Sn}^{\text{IV}}$ , or four hooks.

Now, although tin remains untarnished on exposure to the air, its salts, as, for instance, a solution of stannous chloride ( $\text{SnCl}_2$ ), will absorb oxygen and stannic hydroxide ( $\text{Sn}(\text{OH})_4$ ) is formed; and if we bring ammonia into this solution, there is precipitated out stannic acid,  $\text{H}_2\text{SnO}_3$ . This loses water and goes back to the anhydrid, stannic oxide,  $\text{SnO}_2$ . Then if we fuse this with caustic soda we have:



There is another stannic acid, but we shall not consider it. What I ask you to do is to look back and see how this metal forms salts with acids, principally as a base with two equivalents for combining, and then, after a little legerdemain with its chloride, comes out in the stannic form with four hooks, oxidizes, and proceeds to do business as an acid.

Of course, truth is relative, and so are acids and bases. Ammonia is not a very strong base, and therefore there is no stannate of ammonium. On the other hand, sodium is much more alkaline than tin, and so we have the stannate of sodium. Why weak nitric acid should make a nitrate of tin (stannous

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nitrate) and strong nitric acid should oxidize, is one of those things that are easier to remember than explain. We know, however, that nitric acid is a great oxidizing agent.

Stannous chloride,  $\text{SnCl}_2$ , is a white salt used in the textile industry and especially in dyeing. It is also used for weighting silks, and here again we have trouble. Fire insurance men know that silks heavily weighted with chloride of tin are liable, under certain conditions, to spontaneous combustion. We get an intimation of this in the action of the chloride above referred to, which absorbed oxygen, producing stannic hydroxide and then stannic acid. The fire starts in that disposition to oxidize.

Stannic chloride,  $\text{SnCl}_4$ , is formed by the action of chlorine upon stannous chloride  $\text{SnCl}_2$ , and is a fuming liquid.

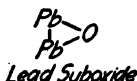
There are two sulphides:  $\text{SnS}$  and  $\text{SnS}_2$ , the stannous compound being a brown, smeary mess, while the stannic sulphide is a yellow, crystalline body used as "mosaic gold" and "bronze powder."

The world's output of metallic tin amounted to 120,400 tons in 1914. This is, of course, mainly consumed in the manufacture of tin-plate, an important industry in this country and in Wales. At the present time tin ore, cassiterite from Bolivia, is being smelted in the United States; the Straits Settlements, however, are the world's principal source.

**LEAD.**—When you come right down to it, some metals are no better than nitrogen in the way of being plain-spoken and easily understood. Lead is more dependable than tin in its chemical reactions, and yet it is full of tricks. Its valency—that is, its number of bonds for combining—is like that of tin: some-

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times there are two and sometimes four. Having settled upon this, we shall shortly have to consider lead suboxide,  $\text{Pb}_2\text{O}$ , and unless we want to guess that the molecule is a kind of triangle with two lead atoms hooked together in a way that they show no disposition to unite—



we had better pass over the matter on the ground that this is not the proper place to discuss it.

Lead is found usually as the sulphide in a mineral called galena or galenite, so we might well say that the inner significance of Galena, Illinois, is sulphide of lead. The ores are roasted and smelted somewhat as tin and zinc, and yet with enough differences to make them subjects of separate and special studies.

Lead is a blue-gray metal with a bright luster when freshly cut, which quickly grows dull on exposure to the air. This is probably due to a thin film of an oxide which in time becomes a carbonate. Perfectly dry air and water that is free from dissolved air leave it bright—have no action upon it. It is not tough enough to be drawn into wire or hammered into thin foil, but it may be rolled into sheets of foil and pressed into pipes. If lead filings are compressed under a pressure of thirteen tons per square inch, they will form into a solid block as though they had been melted; and if a pressure of thirty-three tons per square inch is brought upon the metal, it seems to liquefy.

If lead is brought into contact with water which holds carbon dioxide in solution and is nearly free from other bodies, as, for instance, rain-water, a soluble carbonate of lead may be formed. This is dan-

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gerous, and if the water-supply of a town is pure and free from hardness it is sometimes necessary to filter it through limestone or chalk to give it sufficient hardness to avoid the formation of the poison from lead pipes. Hard water forms a coating of insoluble salts which cover it and avoid the danger of poisoning. All lead salts are poisonous.

Lead poisoning is a mean affliction, and is cumulative—that is, we never get used to it—and as we are more and more subjected to it the worse it grows. If rain-water is used for drinking, it is better not to have the gutters and leaders made of lead; and, owing to the solvent action of organic acids upon it, if cooking-vessels are plated with tin containing lead, they may contaminate the food with poisonous lead compounds.

There are chlorides and iodides of lead, but they are not very important, whereas its oxygen compounds are five in number and are widely used.

Lead suboxide,  $Pb_2O$ , is supposed to be the thin coating formed on lead when exposed to the air. It may be produced by heating certain organic salts of the metal, and is a dark-gray powder.

Lead monoxide, or litharge,  $PbO$ , is a reddish yellow crystalline body, sold as a yellow pigment. It is also used in glass-making.

Lead sesquioxide,  $Pb_2O_3$ , is an orange-yellow powder that is not very stable, going over into the monoxide and dioxide.

Lead tetroxide,  $Pb_3O_4$ , red lead or minium, is formed by heating lead monoxide or white lead in the air to  $350^{\circ}$ – $500^{\circ}$ . It is a scarlet powder which, on heating, grows deeper in tint, then violet, and finally black, becoming red as it is cooled off. It is the very opposite of almost everything else in that, instead of grow-

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ing red-hot, it becomes black-hot and red-cold. Hydrogen sulphide in the air will also turn it black. It is not as stable a red as vermilion (mercuric sulphide) because of this quality, but it is an excellent paint for iron. The reason why it is better as well as cheaper for ironwork is because the iron displaces the sulphur in mercuric sulphide, but it is unable to lure the sulphur away from its combination with lead in this form.

Lead dioxide, sometimes called lead peroxide,  $\text{PbO}_2$ , is a brown powder and is an oxidizing agent. For this reason it is not very stable. If a stream of hydrogen sulphide is brought into contact with it, the gas will catch fire.

About 513,000 tons of lead were produced in the United States in 1914. The lead ores of the Mississippi Valley and a little of the ore received from certain of the Western States are almost free from silver, and the metal produced from them is known as "soft lead." Over 200,000 tons of soft lead were produced in 1914.

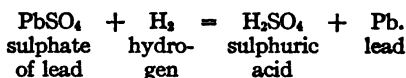
The greatest uses of the metal are for protection against sulphuric acid, as in acid-chambers and lead-lined tanks, and for plumbers' piping and supplies.

*The Storage Battery.*—Improvements in storage batteries provide for the use of other metals than lead, but lead is the old standard, and with it the principle may be explained. If two corrugated lead plates are covered with a paste of litharge,  $\text{PbO}$ , and dipped into a 20 per cent. solution of sulphuric acid, the litharge on the plates is converted into the sulphate  $\text{PbSO}_4$ . Now if you pass an electric current through the cell, hydrogen is evolved at one pole and oxygen at the other. You may remember that by a current

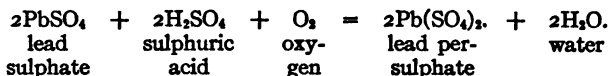


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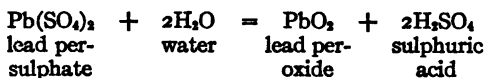
of electricity through water containing an electrolyte like sulphuric acid the water is decomposed into its elemental parts, the hydrogen going to one pole and the oxygen to the other. Then, having the thin coating of lead sulphate on each pole, let us see what happens: the hydrogen takes the place of the lead in the sulphate, producing a gray film of spongy metallic lead and sulphuric acid. Here is the reaction:



At the anode, or other pole, the oxygen goes to work also; it transforms the lead sulphate,  $\text{PbSO}_4$ , into lead persulphate,  $\text{Pb}(\text{SO}_4)_2$ , with the help of the sulphuric acid present:



This persulphate is acted on by the water, is hydrolyzed into sulphuric acid and lead peroxide—here we have it:



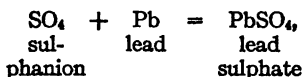
—and a dark-brown film of the lead dioxide (or peroxide) is formed on the lead plate. Thus we have spongy metallic lead on one pole and brown lead peroxide on the other, and we can shut off the current. The battery is "charged."

Now let us hark back to the ionic theory, which we considered in the early part of the book, and remember that sulphuric acid is an electrolyte and that

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it splits up into ions with positive and negative charges. These ions, hydrogen and  $\text{SO}_4$ , are skimming about, ready for business. The hydrogen ions travel over to the plate with the brown  $\text{PbO}_2$  powder, and they reduce the lead peroxide to lead monoxide, or litharge, again.

Observe:  $2\text{H} + \text{PbO}_2 = \text{H}_2\text{O} + \text{PbO}$ , which brings us back just where we started, except for the fact that the hydrogen ions gave up their positive charge as soon as they struck this pole, and for every molecule of  $\text{PbO}_2$  reduced to  $\text{PbO}$  there are two positive charges of electricity delivered at that pole. On the other hand, the  $\text{SO}_4$  ions travel over to the other pole and convert the spongy lead to the sulphate, thus:



and the  $\text{SO}_4$  ions, giving up their negative charges upon the plate, you have one pole with a positive charge and the other with a negative charge. Now, as the two leaden plates which serve as poles are connected by wire, if you measure the current you find it to be about two volts, and this will continue for about twelve hours. The current continues as long as there is any of the brown lead peroxide left on one of the plates. When this is gone the battery is said to be discharged.

The situation is then the same as before. The lead oxide, or litharge, left by the hydrogen is converted into sulphate of lead by the sulphuric acid, and we have once more the sulphate on both poles. Then the battery is "charged" again by the introduction of an electric current. In other words, it is fully charged when lead peroxide covers one pole and spongy lead

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the other. It is discharged when sulphate of lead covers both poles.

There are hydroxides of lead which may be regarded as combinations of the monoxide (litharge) with water, and which with acids produce lead salts. But with the more alkaline metals sodium and potassium, they act as an acid toward them, and then we have lead behaving like tin and producing plumbic acid and forming the plumbates of Na and K.

There is a whole range of lead salts in which lead is the base. The nitrate is soluble, the carbonate is not, whereas the bicarbonate is and the acetate is very soluble. Because of its sweetish taste the acetate is called sugar of lead. This is a misleading name, for it is not a sugar in any sense, as we shall observe in organic chemistry. Like all lead salts, it is a rank poison. The sulphate is insoluble, as is also the sulphide, which, as galena, is a crystalline black rock, but which, precipitated out of a solution, is a black, smeary mass. This is the stuff that develops in oil paints when the artist has not known better than to mix vermilion (mercuric sulphide) with white lead, and the lead drives out the mercury, taking its place as lead sulphide.

White lead is not the insoluble carbonate, but rather a basic carbonate or a mixture of lead hydroxide and carbonate. The following formula would about represent it:  $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$ . There are many different ways of making it. The oldest is called the Dutch process, in which lead disks, or "buckles," are placed in earthen pots that contain a little dilute acetic acid. These are piled up in tiers embedded in tan-bark or manure in such a way that the air flows over them. The tan-bark or the manure ferments and produces carbonic acid, which in turn forms the

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carbonate of lead in the presence of the acetic acid which seems to act as a catalyst. The process takes ninety days, whereas other processes are very much shorter. It seems absurd to spend so much time over a problem that should be simple, and those who make white lead by a shorter process say their product is just as good. The Dutch-process people, on the other hand, declare that it is not, and that the proof of their contention is their much larger sales. We can very well afford to let them fight it out. If the Dutch-process product really is better, it may be shortened some day with the help of colloidal chemistry.

## XVI

### STILL MORE METALS

The Grand Old Tramp Who Left His Mark—Cobalt—Nickel—Chromium—The Goldschmidt Process—Thermit—Chromium in Combination—Tanning—A Lopsided Leather Test with Policemen and Letter-carriers—Manganese—Molybdenum—Tungsten—Uranium

ONE of the fathers of chemistry was old Philippus Aureolus Paracelsus Bombastus von Hohenheim, known as Paracelsus. He was born in Switzerland, in 1493, and died in Salzburg, in the Austrian Tyrol, in 1541. "He lived," says one writer of him, "like a pig, looked like a drover, found his greatest enjoyment in the company of the most dissolute and lowest rabble, and throughout his glorious life he was generally drunk." Another writer says: "It is true that his life offered a strong contrast to his mentality, but he was a man of noble character and intentions, a Christian humanist and ambulatory theosophist, who hoped to inspire mankind with a love of conscientiousness and veracity, and to restore the suffering to health." Take your choice. I wish we had space to devote a whole chapter to the old boy who was active as a teacher, chemist, physician, writer (over a hundred books are attributed to him), and as a tramp.

In working over copper and other metals he was very much annoyed by two bodies that he could not succeed in separating and yet that were neither cop-

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per nor iron. Sometimes they were present and again they were not, and they behaved in a way that was no less than devilish. Now in the Harz Mountains they have been familiar with evil spirits for many centuries, and among the several varieties that enjoy the pursuit of happiness, both there and elsewhere, is a species called kobolds—which at times I confess I am disposed to believe in myself. They are said to be less than three inches high, usually, and they can get in and out of any place. It is their especial pleasure to roll your collar-button under the bed, to move your chair around so that you may stub your toe against it if you get up during the night, to work your penknife, keys, watch, and other valuables into upholstered recesses of your sofa or easy-chair, and, generally, to hide things. Another species of devils, less clearly defined, were known as little Nicks or Nickel. So old Bombastus referred to these two metals by the names that we know as cobalt and nickel to this day.

They are not very rare, and may be separated without much difficulty by electrolytic processes by those that know how. Both are silvery white, cobalt having a pinkish tinge and nickel a faint yellowish hue. Or, lest your eye betray you, let us give the definition of another writer and say that cobalt is slightly bluer than nickel. The latter definition is more evident to me. Cobalt is less tough than iron and no great commercial use has thus far been found for it as a metal. It makes two series of compounds, with two bonds and with three. Cobaltous chloride ( $\text{CoCl}_2$ ) crystallizes in light-red crystals ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) that form a nearly colorless solution, but when dehydrated become deep blue. By this means an invisible ink is made which does not show until the paper is

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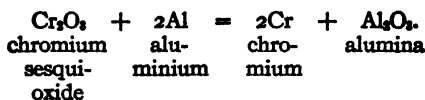
heated, and thus the water driven off. Then it becomes blue. Left to itself it gradually takes on water from the air and becomes invisible again. A sort of cobalt glass is made by fusing sand, cobalt oxide, and potassium nitrate, which, when powdered, becomes a blue pigment called "smalt," and is used in china-painting and by artists. Thénard's blue is made by calcining cobalt oxide with alumina.

Nickel, on the contrary, is very widely used. It is produced in great quantity at Sudbury, Ontario, and is found along with copper and iron. A mixture of the three metals is called Monel Metal and has great strength and endurance. It is used for propellers of steamships and a number of other purposes. Nickel alloyed with steel, which makes it very hard and tough, is used as nickel-steel for parts of machinery designed to withstand continuous wear and shocks, and in the manufacture of armor, burglar-proof safes, etc. As nickel does not tarnish readily in the air and is as easy to apply as silver, it is largely used in electroplating. Nickel coins are three parts copper to one of nickel.

Chromium is another steel-gray metal which does not occur free in nature, but usually as an ore called chromite, which is a chromite of iron  $\text{Fe}(\text{CrO}_2)_2$ , or as an oxide mixed with earth and known as chrome ocher. Traces of it occur in emerald, jade, serpentine, etc. The usual method of preparing the metal is by the Goldschmidt process, whereby the inventor, Prof. Hans Goldschmidt, produces at his works at Essen about 100 kilos (220 pounds) at a charge. He mixes carefully powdered metallic aluminium and chromium oxide and fills a refractory clay crucible two-thirds full with it. A mixture of boron peroxide, which gives off oxygen very easily, and more aluminium or magnesium

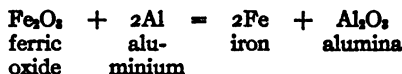
## EVERYMAN'S CHEMISTRY

powder is placed in a little heap over the center of the crucible and the whole covered with a protective layer of feldspar. A piece of magnesium ribbon is stuck into the pile of boron peroxide and aluminium or magnesium powder, and when the crucible has been properly placed on a sand-bath, and the operator has provided himself a good runway to avoid accidents, the magnesium ribbon is ignited. In the reaction which follows a temperature of  $3,000^{\circ}$  centigrade is reached:



When the crucible is cold the chromium is found at the bottom, while the slag is fused alumina, a kind of artificial corundum. A number of other metals, including manganese, vanadium and tantalum, may be produced in the same manner, as we shall see.

The reaction is also the principle of Goldschmidt's thermit, which is used for welding shafts, rails, and broken pieces of heavy machinery. The crucible for this purpose is cone-shaped, and the charge is iron oxide with aluminium powder, because molten iron is what is wanted. The reaction then is:



The ends of the broken shaft or part are heated and brought together and a mold built around the place to be welded. Then the thermit cone is placed above the opening in the mold, little end down, and the reaction is started. The molten iron runs right in where it is needed, through an opening at the point of the cone, making a complete joint.



## STILL MORE METALS

In the steel industry the metal is usually introduced in the form of ferro-chromium, which is made by smelting chromite in an electric furnace. It contains over 60 per cent. of chromium and less than 2 per cent. of carbon. Steel with  $1\frac{1}{2}$  or 2 per cent. of carbon and  $2\frac{1}{2}$  to 4 per cent. of chromium is drill-proof; it cannot be worked with ordinary hardened tool-steel. Chrome-nickel steel is used for armor-plate.

Stellite is the trade name for an alloy of chromium and cobalt with manganese and molybdenum in varying proportions. It is very hard, is not affected by high temperatures and does not tarnish in the air.

Chromium combines with oxygen and hydrogen to a series of oxides and hydroxides that are mild acids and bases, very much according to the company they are in. They are employed in making paints, of which the best known is lead chromate or chrome yellow.

Dichromate of potash,  $K_2Cr_2O_7$ , is a great oxidizing agent, going over on slight provocation to  $Cr_2O_3$  and letting loose a lot of oxygen. This is used in bleaching, dyeing, calico-printing, and in chemical industry. It is employed in photography, because gelatin, mixed with it, becomes hard and insoluble in the light. If a pigment is mixed with gelatin and dichromate of potash in the dark, and, still in the dark, applied to paper and put under a photographic negative and then exposed to the light, the gelatin which holds the pigment in suspension will glue itself on, hard and insoluble, to the paper wherever the light has struck it. Then if, back in the dark-room, the paper is removed and washed, everything will wash off except where the light has struck through the negative. That is the way the beautiful carbon prints are made.

This effect of dichromate of potash on gelatin gives

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a hint of the reason for chrome tanning. Tanning is still more of an art than a science, as witness the use of dog dung for making morocco and horse grease for crown leather. There is no reason why such materials should not be employed, but they are likely to indicate that the chemical reactions are not yet thoroughly known. The skins of animals consist in general of two layers, of which the outside, or epidermis, is made up of simple, hardened, and flattened cells, while underneath these the cells are soft and spherical and are referred to as the mucous layer. The hardening of the gelatinous mass and rendering it so that it will not putrefy is the main business of tanning. I take it that by this time you will have observed that the chemistry of tanning is a very complex subject and that many of its problems have not yet been mastered. We shall not even take it up in organic chemistry. The tannins, which we shall merely note in passing later, are found in many woods and barks and reach the tanner either as wood or bark or in the form of extracts. But the shorter process of mineral tanning has come into frequent use, and here the chromium salts lead. It has become a great industry, especially in the preparation of upper leathers. There is a method of combined chrome and extract tanning that produces sole-leather of remarkable endurance. A considerable number of policemen and letter-carriers were shod with one boot soled with the best oak-tanned sole-leather available, and the other with that made by the new process. The new-process leather outlasted the old in the ratio of nearly three to one. Why the new method has not come into use would be a mystery if it were not for the fact that inventions that offer no immediate profits to industry are often hard to get started. When the general

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public is better informed about chemical processes we shall not have to wait so long for improvements.

Now let us note a few more metals that are frequently heard of in connection with the steel industry. Some have other uses also.

Manganese is a gray metal with a reddish tinge that rusts in moist air like iron, and is occasionally found with that metal in the form of one of its many oxides. It is brittle and harder than iron, and is most easily prepared, like chromium, by the Goldschmidt process. It is frequently brought upon the market in the form of ferro-manganese, which contains it in varying proportions. Ferro-manganese is needed to reduce the iron oxides in Bessemer-steel converters, in which the manganese picks up the oxygen from the iron and goes off with it into the slag. Alloyed with steel, manganese makes it very hard and free from air-holes. This is frequently used for burglar-proof safes, dredge-pins, crusher-plates for ore-mills, and the like. Manganese is also alloyed with other metals, chiefly for its hardening effect.

Chemically it is interesting—and perplexing. In the matter of valence it sometimes has two, sometimes three, and at others four, six, or even seven bonds, or hooks, for combining. It forms a whole series of oxides, of which the lower ones are basic and the higher ones acid in their reactions. Permanganic acid makes salts with the alkalies that are great oxidizing agents, the permanganate of potash being often used in the laboratory and in medicine. Its crystals are purple with a greenish luster, but in solution it is deep red. When the higher oxides of manganese are heated they give off oxygen and revert to a lower type. We have already noted the use of manganese compounds in glass-making.

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Molybdenum is found usually as a sulphide,  $\text{MoS}_2$ , known as molybdenite, and as wulfenite, a molybdate of lead,  $\text{PbMoO}_4$ , but chiefly as the sulphide. The pure metal is softer than steel and yields readily to forging and welding. But when it is added to molten steel in very small quantities, it is reported that molybdenum nearly doubles its tensile strength, adds to its capacity for elongation, to its toughness, its fineness of grain, and retention of magnetism. It has been used by the Germans for lining their enormous howitzers, while projectiles of molybdenum steel are found to have great power of penetration. It is also desirable for strong wire, rifle-barrels, propeller-shafts, and wherever great strength is needed.

Tungsten is very like molybdenum in its compounds, and it has an effect similar to that of molybdenum when alloyed with steel. It is found in the mineral scheelite, which derives its properties from tungstate of calcium,  $\text{CaWO}_4$ , and wolframite,  $\text{FeWO}_4$ . The symbol W is from the German name of the element, wolfram. The very weak tungstic acid combines with strong alkalies, and of these an interesting use has been found for the tungstate of sodium,  $\text{Na}_2\text{WO}_4$ . Cotton cloth soaked in a solution of this will not burn with a flame, but at most only smolders away slowly. Lead tungstate is a good white paint, while tungsten trioxide is a canary-yellow pigment. The greatest use for the metal is for filaments in electric-light bulbs.

Uranium is found in pitchblende, and, like manganese, molybdenum, and tungsten, is indefinite in valency. Sodium diuranate,  $\text{Na}_2\text{U}_2\text{O}_7$ , is known as uranium yellow, and is used for coloring glass and for pottery glazes. Just now there is considerable discussion going on as to the merits of alloys of steel with uranium.

## XVII

### SOME OF THE RARER METALS

Silver—Its Many Different Colors—Chemistry—Coinage—Electroplating—How to Clean Silver—Silver Salts—Photography—The Great Domain of the Chemistry of Light—Gold—All Gold Does Not Glitter—Metallurgy—Gold when It Is Red—Some Figures About It—Platinum and Its Family—Mercury—Compounds—Radium

**S**ILVER is valuable because it is rare, but if it were not so rare we should use a great deal more of it. It is a better conductor of heat and electricity than copper, and it is "noble" in that it is more enduring than iron, copper, or other metals—that is, it is not so easily oxidized. It occurs in a free state in nature; occasionally it is found in large masses, crystallized in cubes—which fill the miner's heart with joy. More frequently, however, it occurs with copper and other metals as the sulphide,  $\text{Ag}_2\text{S}$ , called argenite.

Its use is older than history. The Phoenicians are supposed to have derived their great wealth of it from Spain and Armenia. It is a white, lustrous metal, but light reflected back and forth from its surfaces many times is yellow. Very thin layers of it have a blue tint. The vapors of it are green. Powdered silver is gray and has an earthy appearance. It is highly malleable and ductile. The air does not affect it unless it has hydrogen sulphide,  $\text{H}_2\text{S}$ , in it; then it is

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blackened, owing to a thin layer of silver sulphide,  $\text{Ag}_2\text{S}$ , in which the silver has replaced the hydrogen.

Dilute sulphuric acid does not affect it, but hot concentrated sulphuric acid produces silver sulphate,  $\text{Ag}_2\text{SO}_4$ . Hydrochloric acid acts slowly upon it until a high temperature is reached, when the insoluble silver chloride,  $\text{AgCl}$ , is formed. Nitric acid, on the other hand, dissolves it readily, hot or cold, strong or dilute, forming nitrate of silver,  $\text{AgNO}_3$ .

The susceptibility of silver to the action of sulphur is so great that even that which is contained in the yolks of eggs will tarnish a silver chafing-dish if left in it any length of time. The sulphur in an ordinary elastic rubber band will quickly tarnish a pocketful of silver coins.

Pure silver is rather soft to be used alone, and for coins it is usually alloyed with copper. Sterling silver, as the British standard of coinage is called, is  $92\frac{1}{2}$  per cent. silver and  $7\frac{1}{2}$  per cent. copper. The coinage of the United States is 90 per cent. silver and 10 per cent. copper. Articles of standard silver may be heated so as to oxidize the copper near the surface, and this oxidized copper is removed by immersing the article in a bath of dilute sulphuric acid, which removes the copper by dissolving it and forming the soluble copper sulphate  $\text{CuSO}_4$ , leaving a thin film of pure silver behind. This is known as "frosted silver." So-called "oxidized silver" is not oxidized at all. Silver ornaments are dipped in a solution of an alkaline sulphide, and this deposits a film of the dark silver sulphide upon the metal, the silver taking up the sulphur according to its wont.

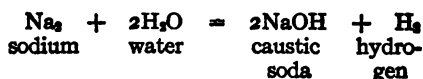
Silver is easily taken out of solution and precipitated upon other bodies by electricity, and silver electroplating is an important industry. Sheffield plate, how-

## SOME OF THE RARER METALS

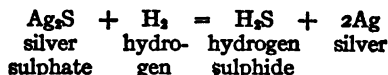
ever, is not silver plated upon a baser metal, but, if genuine, consists of copper and silver sheets that have been rolled together at a little below the melting-point of silver.

To clean silver, the best way is to do so electrically, and this may be done conveniently in any kitchen or butler's pantry. The first requisite is an earthenware pot. Metal will not do. Then put into the pot one or two pieces of zinc or aluminium, such as may be purchased at nearly any hardware-store. One or two pieces of sheet-metal, say four by ten inches, will be enough. Fill the pot one-half to two-thirds full of hot water and add two or three heaping tablespoonfuls each of table salt and of bicarbonate of soda. These are the electrolytes. Then put in the tarnished silverware, and it will grow bright in a little while.

We must go back to the ionization theory to explain this. Both zinc and aluminium are electropositive to silver, and a current is set up between them. The salt, NaCl, splits into sodium and chlorine ions, the chlorine ions going over to the zinc and forming zinc chloride, which goes into solution. The sodium ions go to the other pole, which is the silver articles. Here they act upon water, release hydrogen, and form caustic soda:



The hydrogen just released acts upon the silver sulphide and produces hydrogen sulphide and free silver:



That free silver is now just where it is desired—on the outside of the spoons, or wherever it was before

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it was tarnished. All grease must be removed before the articles are put into the pot.

The preparations that are sold that plate silver on places where brass or base metal is exposed contain a little silver in a condition of chemical instability. When it meets the baser metal an exchange of acid and base occurs, the silver being deposited upon the vessel in the place of the copper taken up by the former silver salt solution.

Cyanide of sodium and of potassium have the faculty of making a soluble silver salt. It is not silver cyanide,  $\text{AgCN}$ , which is insoluble, but a double salt, the sodium (or potassium) silver cyanide,  $\text{Na}.\text{Ag}(\text{CN})_2$ . These cyanides are so wickedly poisonous that it is no less than a crime to sell them in silver polishes, although they dissolve silver in almost any form, including the black sulphide. Thiosulphate of soda, which the photographic people call "hypo," will also make a complex soluble salt, but not so easily as the cyanides.

Cyanide of soda is largely used in the extraction of silver from its ores.

Chloride of silver is a white, cheese-like mass, insoluble in water, and is formed when a solution of a silver salt and nearly any chloride are brought together. On exposure to the light it turns dark—please mark this, as we shall come back to it presently.

Nitrate of silver may be obtained by treating the metal with nitric acid. It produces colorless crystals which melt at  $218^\circ$  centigrade. It is cast in thin sticks and used in medicine as "lunar caustic" because it combines with albumens to form insoluble compounds. It gets its name from the old term of the alchemists, who referred to silver as luna, the moon,



## SOME OF THE RARER METALS

and had for its sign the crescent. The nitrate is very soluble in water.

There are oxides of silver, but as they are not formed on the heating and exposure of the metal to the air, we shall not discuss them.

Since silver salts are the active agents in making photographic images, let us consider what happens, in a general way, in the making of a photograph. You will remember that silver chloride turns dark on exposure to the light. The bromide and iodide have the same properties, and the bromide has been found the more available. It appears that under the action of light, a subchloride,  $\text{Ag}_2\text{Cl}$ , or a subbromide,  $\text{Ag}_2\text{Br}$ , is formed, but how they hook up this way in the molecule is not clear, since both silver and the halogens are monovalent. But bromine does some tricks for a self-respecting, monovalent element, and we might as well admit that this whole subject of valency, or the number of combining hooks or bonds that the atom of an element has, is full of perplexity. Suffice it to say that silver bromide, which is light yellow when first produced, becomes dark on exposure to the light. The dry photographic plate is coated with an emulsion of gelatin (in a colloidal state, you observe), and the emulsion contains silver bromide in a very finely divided condition. In the case of moving-picture films, thin strips of transparent celluloid are coated in the same way. Now, as the light strikes these plates or films, the bromide of silver is reduced in part, and, *according to the strength of the light*, from silver bromide,  $\text{AgBr}$ , to silver subbromide,  $\text{Ag}_2\text{Br}$ . The negatives still have a milky white appearance. They are now put into a developing bath, and the purpose of this is to reduce the silver subbromide to metallic silver. The developers are mild reducing agents—ferrous sul-

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phate, pyrogallol, or organic compounds which have trade names such as hydroquinon, metol, etc. What they accomplish is to take up that bromine in the  $\text{Ag}_2\text{Br}$ , but not that in the  $\text{AgBr}$ , of which, of course, a great deal is left on the plate. Then, without letting the light reach the plate, it is further immersed in a bath of "hypo," which is a solution of sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3$ , and this dissolves out *all* the unaffected silver bromide,  $\text{AgBr}$ .

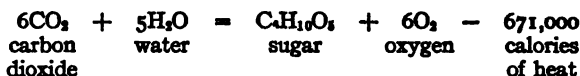
There is now nothing left in the plate but films of silver, with particles so close together as to appear black where the light has been strongest, particles at greater intervals apart in the shadows, and nothing at all where there was no light to change the silver bromide that was originally put on and later taken off in the hypo (thiosulphate) bath. This is a negative—dark where the original was light and light where the original was dark. After it has been dried it is placed upon paper that is also coated with a somewhat similar solution of gelatin and silver bromide and subjected to the light. This shines through the light spots in the negative and makes the corresponding places dark on the paper. And that is the photograph.

Photochemistry is a very big subject and goes much further than taking photographs. It has to do with the chemical action of light—and of radiant heat obtained from the rays of the sun—and there are whole Americas to be discovered within that domain.

Let us consider what plants do by means of photochemistry and take a hint or two from them. There are two bodies in the leaves of plants called chlorophyl and protoplasm. Never mind the chemical formulas for them; it would be too much like guessing for us. But there they are. They have the power of taking up carbon dioxide,  $\text{CO}_2$ , from the air and water which is

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brought to them in rain and dew, and converting them into sugar, starch, and cellulose. Starch, which is needed to feed the germ in the seed cell, and cellulose, of which all its cells are made, are in effect bunched or polymerized molecules of sugar. A plant can do that, and we can't, but that is not to the point just now. We are discussing the photochemical activities of chlorophyl and protoplasm. Let us write out what happens to the water and carbon dioxide:



If there is a loss of 671,000 calories in this reaction, where did the plant get the heat to supply it? If the cost of the reaction is 671,000 calories, you must supply them if the reaction is to take place. It gets this heat from the sun.

Therefore every stick of wood we burn is energy stored up by the sun. The sun furnished the heat to cause the reactions. In other words, to make the wood out of water and  $\text{CO}_2$  gas it took a great deal of heat. Now, to turn that wood back to water and gas, the same heat is given out. That is the way we get our sunlight back when we sit around the fire. But this is not all. Except the little work done by water-power (and the water was lifted by the sun), all the energy of men and animals comes from this stored energy of the sun. All our food is from that source. In every movement, every thought, we avail ourselves of energy gathered from the sun.

Now observe the significance of photochemistry. We have touched one little edge of it in making pictures. We find that ultra-violet rays of light destroy bacteria. In chlorination processes, getting chlorine

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into combination when needed, it is likely that light will play a great rôle. Do you grasp what is done in this? *It is taking power direct from the sun.* It is getting the effect direct instead of waiting throughout eons of years for energy to be stored by means of chlorophyl and protoplasm into wood and wood to be reduced to coal. It is doing ourselves what nature does for us. It is a direct reaction gathered in from space. How far shall we be able to avail ourselves of this illimitable power? Who will grasp this Might of Day and master it?

GOLD.—The robber baron would not associate with common, honest folk; he held aloof from them and would have no dealings with them save to command. So he was called noble. Gold long antedates the robber barons, but it obtained its title to nobility in the same way. It does not combine with free oxygen or even hydrogen sulphide. Acids do not attack it as a rule, and so it achieved a grand reputation as the aristocrat of all the metals. Another likeness to the robber barons of old is that the gold strain is found everywhere; there are traces of it in sea-water to the extent of about three and one-half grains to the ton. Granite contains about one part in 7,000,000,000, and clays, iron pyrites, and nearly all silver, copper, zinc, lead, bismuth, tellurium, and antimony ores contain it.

In the mass gold is yellow, but light, reflected from its surfaces many times before it reaches the eye, is red. Gold-leaf is green or blue in transmitted light, and if precipitated in a very fine state of subdivision the tint varies from red to dark brown. So some gold does not glitter.

The practice of chemistry is a sport, very like hunting wild game. As soon as its ways are well

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enough known the game is likely to be brought down. Here is gold with all its far-famed nobility, and yet even the medieval alchemists found a solvent for it in what they called *aqua regia*, a mixture of nitric and hydrochloric acids. Nitric, hydrochloric, or sulphuric acid alone does not affect it, but that *aqua-regia* mixture will dissolve it.

Gold chloride is soluble, and by treating this with an oxidizing agent oxides of gold are formed. They are not very stable, and so far no great use has been found for them, but there they are.

Gold is obtained in a number of different ways. From alluvial deposits the very heavy metal is separated from the gravel. Whether this is done in pans or "cradles" by hand, or in great sluices, the principle is the same. The gold stays while the gravel is washed away. In vein-bearing mines the gold-bearing quartz is blasted out and crushed to a fine powder in stamp-mills. Then the powder is floated in troughs as "slime" over copper plates amalgamated with mercury. Gold is very soluble in mercury, and this takes up the particles as the slime floats on. The gold amalgam is scraped off and the mercury removed by distillation. That is the amalgamation process.

The chlorination process is used in connection with sulphur-bearing ores such as pyrites. The ore is first roasted, then wet, and the gold is extracted with chlorine which goes into solution. The chloride of gold is precipitated by means of hydrogen sulphide, which brings the gold, but only the gold, back to the form of a sulphide again. Then the sulphur is roasted away and the gold remains.

The cyanide process provides that the powdered ore be leached with a solution of cyanide of sodium, which dissolves the gold as the double cyanide,

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$\text{NaAu}(\text{CN})_2$ , and the gold is precipitated out by the addition of zinc shavings which take its place in the soluble cyanide.

Colloidal gold is a suspension of particles of this heavy metal so small that the bombardment of the molecules of the liquid keeps them in suspension. It is made as follows: A solution of about one-hundredth of one per cent., or less, of gold chloride is made slightly alkaline by adding magnesia. Then a few drops of a mild reducing agent that will take up the chlorine, such as oil of turpentine or carbon monoxide, is added until the solution acquires a ruby-red color—if it does. The thing is tricky. This is Faraday's gold, as it is sometimes called, or colloidal gold, and the particles are so small that they will pass right through filter paper. It is red because, as we have observed, light reflected backward and forward from many surfaces of gold is red; and this condition will last, with the particles constantly dancing about, as may be seen with the ultra-microscope, for an indefinite time. But as soon as you add an electrolyte, such as common salt or sulphuric acid or caustic soda, the red color changes first to blue, then to violet, then to black, and finally the gold particles, having coagulated, settle down on the bottom of the vessel.

Gold is too soft to be used in a pure state, so for coinage in Great Britain 22 carats, or 91.66% per cent. gold and 8.33% per cent. copper are used. The mint at Sydney, Australia, uses silver instead of copper, so that the Sydney sovereign is of a greenish yellow. In the United States, France, and Germany an alloy of 90 per cent. gold and 10 per cent. copper is used.

Gold is the standard of money, and it is not a very good standard because it fluctuates in value itself. The world's production of gold in 1915 was 22,758,808

## SOME OF THE RARER METALS

fine ounces, valued at \$470,466,212, of which the United States produced 4,887,604 fine ounces, valued at \$101,035,700. The world's industrial consumption of gold in the same year was \$66,651,860, of which the United States consumed one-half, or \$35,736,700 worth. The world's production of gold for the ten years previous to 1916 in millions of fine ounces has been, respectively, 56, 56, 52, 54, 57, 60, 63, 67, 72, 75.

PLATINUM is one of a group of six metallic elements known as the platinum elements, and they are ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt). They are all silvery white and lustrous, chemically inert, and exceedingly rare. The great value of platinum is in part due to the fact that it is not attacked by air and strong acids and the very high temperature at which it fuses, so that chemists need dishes and crucibles made of the metal. On the other hand, alkalies do attack it, and it makes alloys with other metals like lead, silver, and zinc, so that the chemist does not like to let the laboratory boy make free with his expensive platinum ware. It has about the same coefficient of expansion as glass, so that it is fused in glass to make gas-tight joints. Alloys of cheaper metals have, however, been devised which also accomplish this purpose.

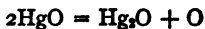
When platinum is precipitated from solutions of platinum tetrachloride,  $\text{PtCl}_4$ , a velvety black powder of pure platinum is obtained which is called platinum black. When ammonium chloroplatinate is calcined the metal that remains behind resembles coke in appearance and this is called platinum sponge. If asbestos is soaked in  $\text{PtCl}_4$  and ignited, the asbestos permeated with platinum is called platinized asbestos. These are the forms in which it is frequently used in

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industry. In finely divided states all metals of this group have the faculty of absorbing vast quantities of certain gases; of drawing a film of the gas to surround every particle. This seems to be the reason why they are of great value in catalysis. Platinized asbestos, you may recall, is used as the catalyst in the contact process for the manufacture of sulphuric acid. It is a great pity that these metals are so dear.

**MERCURY.**—You can't pick it up, and that is a good way to prove that it is a liquid. It is useful in amalgamating gold from its ores because gold is very soluble in it, and of course it is used for thermometers and barometers and in certain chemical industries. A liquid over thirteen times as heavy as water naturally has its uses.

It is found in nature chiefly as the sulphide, and mere heating is enough to drive the sulphur out of combination, leaving the metal free. The sulphide is known as cinnabar and vermilion, and it is a grand red paint unless it comes in contact with white lead, when the black lead sulphide is produced, as we have noticed elsewhere. Mercury has two methods of combining, as monovalent and divalent—that is, with one bond and with two. When one bond is engaged the compounds are mercurous; when two, they are called mercuric. Mercurous oxide is  $\text{Hg}_2\text{O}$ , and mercuric oxide is  $\text{HgO}$ . If the latter is heated we get free oxygen and mercurous oxide:



If mercury is ground up with, for instance, milk sugar it becomes divided into very fine globules, and these have, as we were reminded under the head of colloidal chemistry, a much greater surface in propor-

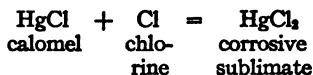


## SOME OF THE RARER METALS

tion to the volume than the metal has in bulk. This is the way blue-pills are prepared, and the mercury has in this form an activity which is lacking in larger masses.

Mercurous chloride,  $\text{HgCl}$ , is calomel.

Mercuric chloride, or bichloride of mercury,  $\text{HgCl}_2$ , is corrosive sublimate. The relation here is a little too close for safety, because either salt may be prepared from the other. For instance, like silver chloride, the mercurous chloride (calomel) is darkened by light, and chlorine is liberated, but it proceeds to abuse its freedom by turning part of the calomel into corrosive sublimate:



Mercurous chloride is used in medicine because it stimulates certain organs in producing secretions, but care must always be taken that it does not go over to the mercuric form and thus become the poisonous bichloride.

Fulminate of mercury is obtained when mercury is treated with nitric acid and alcohol is added to the solution. The formula is  $\text{Hg}(\text{ONC})_2$ . It decomposes suddenly when struck, and is used in making percussion caps. It is a white precipitate.

The thiocyanate is another interesting salt. Potassium thiocyanate,  $\text{K}(\text{SCN})$ , will precipitate it from a solution of a mercuric salt. When formed into little balls and burned in the air they have a voluminous ash and are known as "Pharaoh's Serpents' Eggs."

**RADIUM.**—In 1896, Becquerel discovered that a photographic plate inclosed in an envelope of black paper which keeps out the light was affected as though light

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had struck it when a compound of uranium was brought into contact with it. He also discovered that the air in the immediate vicinity of a compound of uranium became a good conductor of electricity—became ionized—whereas otherwise it was not. Now this quality of uranium compounds is proportional to the amount of uranium in it. But uranium ores were discovered to be four times as active as the uranium itself. This led Professor and Mme. Curie to the discovery that the pitchblende residues from which the uranium had been extracted were also active. After working over a ton of such residues and eliminating that which was not active in this manner, they found the quality to abide in the barium chloride in which they could discover no other element by the ordinary chemical tests, and they found that it was sixty times as active as uranium. The percentage of chlorine was very nearly that to be expected in barium chloride, and yet this was not like any other barium chloride; it had this remarkable photo-activity and it ionized the air so that it became a conductor of electricity. So this man and wife in their laboratory purified and crystallized and recrystallized their barium chloride until they separated out a new compound that contained less chlorine proportionately than barium chloride and showed an entirely different spectrum. It proved to be bivalent, to have an atomic weight of 226.5, and took thereby a vacant place in the periodic table. Its activity from a photochemical standpoint and its capacity to ionize the air proved to be three million times as great as that of uranium. So they called it radium, from its disposition to emit rays.

Now the chemical reactions of barium and radium chlorides are so much alike, and they are always found together, so that the only way to get them apart is

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by taking advantage of their different degrees of solubility. By means of electrolysis a minute quantity of a white metal, which is radium, has been prepared. It melts at  $700^{\circ}$ , turns black in the air, chars paper, and dissolves readily in water and dilute hydrochloric acid.

The properties of radium which upset so many of the theories in regard to the permanency of matter are due to the fact that it is constantly giving off of its substance with the development of heat. One gram of radium, which is about fifteen and one-half grains Troy weight, would produce the same amount of heat, if developed spontaneously, as would be caused by the combustion of 300 kilograms of hydrogen. Nothing else is known to develop such heat. It comes from the disintegration of the atom. If this could be brought about artificially with other elements, say with carbon, a bucketful of coal would propel a ship across the sea—if the ship were not too big and the sea were not too wide. These rays do all sorts of tricks. They incite luminosity in diamonds, rubies, fluorspar, calcium sulphide, zinc sulphide, and a number of other bodies. Luminous watches and clocks now have the hours painted on with a coating of zinc sulphide with which an absurdly small amount of radium bromide has been mixed. In the dark they glow with a greenish light. If a tube of radium salt is held before your forehead, you can see the light through your closed eyelids—but this is not an experiment to be recommended. If you carry a tube of radium bromide in your pocket for a few hours you will suffer from painful sores that are very slow to heal. The rays discolor paper, turn oxygen into ozone, reduce bichloride of mercury ( $\text{HgCl}_2$ ) to calomel ( $\text{HgCl}$ ), and are about the busiest mites in nature.

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Three kinds of rays are given forth; and if a strong magnet is held above a piece of radium salt, *alpha* rays will go to the negative pole, being positively charged, *beta* rays will go to the positive pole, being negatively charged, and the *gamma* rays are not affected—they go right on. For this experiment the salt is put into an open lead container, as lead is more resistant to the rays than other bodies.

The alpha rays are projected at a velocity of 20,000 miles a second, but they have slight penetrative power. Even the resistance of a few cubic centimeters of air is too much for them. They appear to be positively charged electrons.

The beta rays appear to be negatively charged electrons, and have more speed than the alpha rays. They are projected from the radium salt with a velocity approaching 100,000 miles a second. Their properties correspond with the cathode rays of a Crookes tube, but they do not travel quite so fast.

The gamma rays have an intense penetrative power and are very similar to, if not identical with, the Roentgen or X-rays. Tested in aluminium, the penetrative powers of the three types of rays are as follows:

alpha : beta : gamma : : 10 : 1,000 : 100,000.

A great deal has been said about the use of radium in curing cancer. The matter is still in dispute. If the rays are really Roentgen's X-rays, it would seem to be beating a long way about the bush to get them from radium. But this is no place for the discussion. No authority regards radium as a sure cure for all malignant growths.

## XVIII

### CARBON

Diamonds—Graphite and Amorphous Carbon—Moissan's Artificial  
Diamonds—Acheson's Graphite Preparations—Uses of Graphite  
—Lead-pencils—Charcoals—Fuels of Many Kinds—Gas-engines  
—More About Fuels—Different Kinds of Gas—Present Waste—  
Improvements Possible and Desirable—Carbonic Acid, and a  
Few Carbon Compounds

**C**ARBON is by far the most profoundly studied of all the elements and it almost seems as though less were known about it than any other. Of all the many compounds recorded in chemistry, over half of them are combinations of carbon. Everything that has life contains it. The carbon molecule is large—how large is not clear, but it must have at least twelve atoms in its simplest form. Like interesting persons, it is not always the same—it is pure carbon as the diamond, as graphite, and as a black, amorphous powder. Anthracite coal is 75 to 90 per cent. pure carbon, and the rest of it is carbon in combination principally with hydrogen and with minerals, such as lime, etc., which show in the ash. Let us consider first the states or allotropic modifications in which carbon is known in a free state.

The diamond is the hardest substance we know; it will scratch any other surface. In the old adage, "Diamond cut diamond," it is indicated that each both cuts and gives way. It resists the strongest

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oxidizing agents, as, for instance, a mixture of nitric acid and chlorate of potash; and it has no interest whatever in acids or alkalies; they do not affect it. It would appear to be the form that carbon takes on when it wants to be left severely alone, chemically. Of course, the diamond miner may get it and you may buy it in a ring for your wife, and a thief may steal it, all of which does not interest the diamond at all. Chemically speaking, it is being left to itself when it is stolen. On the other hand, if you try to bring it into combination with other elements, it will show how inert it is—unless you know the tricks, unless you are familiar with that strategy which is the substance of research in science. Then you become the master and the diamond is no more inert. In this case, all you have to do is to heat the diamond to redness and dip it into a flask containing oxygen. Then the diamond will burn with a bright flame, just like any piece of coal. Examine the gas that proceeds from this combustion and you prove the diamond to be carbon, for the gas is carbon dioxide,  $\text{CO}_2$ , and nothing else. Lead it through lime-water and down comes the white precipitate of carbonate of lime, or marble. Here is another chance for a modest millionaire to construct for himself a marble gravestone made of lime and diamonds.

If a diamond is subjected to a very high temperature in the absence of air, it turns to graphite. The diamond is a very poor conductor of heat and electricity.

Moissan, a French chemist, made diamonds artificially in 1893 by dissolving pure carbon made from sugar (which is a compound of carbon, hydrogen, and oxygen) in molten iron in an electric furnace at about 3,000° centigrade, and then cooling it suddenly by

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pouring the mass into a hole drilled into a copper block which was cooled, and covering the cavity with an iron stopper. When it had cooled, the metal was dissolved away by an acid, and there remained very small diamonds, precisely like the rough diamonds found in the mines in their crystal form, hardness, etc., and they displayed the same rounded edges and angles. No one has succeeded in producing diamonds of any appreciable size.

Graphite is also crystallized carbon. Unlike the diamond, it is very soft and opaque, and it is a very good conductor of heat and electricity. It occurs in nature and is made artificially by heating Pennsylvania anthracite coal finely powdered in an electric furnace. It has very wide-spread use. Remember, this is carbon, just like the diamond, but there is a difference in the arrangement of the atoms in their molecules. When two bodies differ, there must be an external or internal reason for the difference, whether we know it or not. Graphite is exceedingly inert at high temperatures, and you cannot make Moissan's little diamonds by using graphite instead of sugar charcoal. It will withstand any heat we can produce, and it remains graphite. But if you treat graphite with a mixture of dry potassium chlorate and very strong nitric acid, it turns to a yellow crystalline substance called graphitic acid,  $C_{11}H_4O_6$ , which, when it is heated, decomposes explosively and yields very fine amorphous carbon. It is a little too explosive to encourage close study. The diamond, you remember, is not affected by the same reagents.

One of the greatest uses of graphite is for making pots or crucibles for crucible steel and for other chemical reactions in which high temperatures prevail. Its physical and chemical inertia is what gives it its

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value for this. Another great use is for electrodes for the same reason, in electric steel furnaces and in fixing or combining nitrogen of the air as well as for other purposes in electro-chemistry. Then it is a wonderful lubricant, being as smooth and unctuous as—some men we know. When chemistry grows popular and anybody is referred to as being "as smooth as graphite," we shall know that butter will not melt in his mouth and that he is so oily that he will slip in anywhere and that there is never any squeak or cry when he is having his own way. Dr. E. G. Acheson, who invented carborundum, discovered that by treating finely ground artificial graphite with a solution of tannin or any one of several organic compounds, it takes on such a fine subdivision of its particles that they pass through filter paper and remain suspended when mixed with water or oil. He calls this form "deflocculated graphite," and gave to the mixture with water the trade name of "aquadag." It is used to aid in cutting metals in machine-shops. Mixed with oil, he calls it "oildag," which is a valuable lubricant. A cheap oil mixed with deflocculated graphite will do the work of a high-grade lubricating oil for the same purpose.

Lead-pencils are not made of lead at all. Graphite does the business. The natural graphite is first freed from the mica and sand with which it is usually found, and then mixed with clay that has also been freed from all grit. The mixture is ground with water between millstones and passed between rolls and through a mixer and then squeezed through a die in the form of a rod. This is dried and baked at a high temperature for the purpose of toughening the so-called "leads." They are then inclosed in wood, and there are your pencils. The more graphite in proportion to



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the clay the softer and blacker is the pencil; the greater the proportion of clay to graphite the harder and lighter the pencil. A similar process takes place in hardening the clay in the leads of lead-pencils to that which occurs in making brick; in fact, the lead in a lead-pencil is a mixture of brick and graphite. Nothing happens to the graphite in making lead-pencils; it stays where it is put until it is rubbed off on the paper.

**AMORPHOUS CARBON.**—This is an indefinite name because under it we must consider the approximately but not really pure amorphous carbons such as coke, charcoal, bone-black, lampblack, etc., and go into a discussion of fuels which range from anthracite coal, which contains the most carbon, always mixed with some minerals, over to peat and wood, in which all the carbon is in combination. Pure amorphous carbon is not found in nature so far as the writer knows. Let us first address ourselves to some of the charcoals before we take up the greater problem of fuels.

Wood charcoal is produced by burning wood with the air so shut out from access to the fire that only the hydrocarbons which burn most readily are consumed, leaving the more or less pure carbon, driven out of the cellulose of which the cells of the wood are composed, unconsumed behind. It is very porous and can condense large quantities of gases in its pores. For instance, it will take up ninety times its own volume of ammonia. When heated it will give the gas off again.

What appears to happen is that the gas is adsorbed; that is, that upon every minute filament of the charcoal a coating of the gas adheres.

Some day let us hope that the adsorption of gases

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may lead us into the study and final understanding of the sense of smell. If any one asks us what makes things smell, we must answer that we do not know, but we have this one point—that odoriferous gases seem to be adsorbed by charcoal. This may have been studied at length, but I do not know of it. Smell is the Cinderella of the senses, and we should know much more about it than we do.

Bone-black is obtained by heating bones away from air. It is then treated with hydrochloric acid, to remove the phosphates and carbonates. It has the power of absorbing coloring matter, and many evil-smelling substances from liquids, and also certain salts, as, for instance, the salts of lead. It is also called "animal charcoal," and is used in water-filters and in sugar-refineries to decolorize the sugar liquids. Mixed with linseed-oil it becomes the artist's "ivory black"—except when lampblack is employed in the place of it.

Lampblack is made by burning natural gas or petroleum residue and catching the black smoke. This "carbon black" is chiefly used for black ink and paint.

Coke is the great fuel of the iron and steel industry, and at the mere mention of it we Americans might well hang our heads in shame. To make coke we distil the hydrocarbons out of coal, leaving the comparatively pure, spongy carbon behind. It may be done in two ways—by what are known as beehive coke-ovens, whereby the coke is saved and everything else burned up or allowed to escape; and by by-product ovens, whereby the coke is saved and so are the valuable by-products. These by-products are a vast amount of gas available for power; ammonia, needed as fixed nitrogen in sulphate of ammonia by the farmers; benzol, toluol, and other hydrocarbons available for making

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dyestuffs, explosives, medicines, and a whole list of chemical products, as well as being useful to operate explosion engines in the same manner as gasolene; phenol or carbolic acid for disinfecting and for chemical manufacture; tar and pitch for roofs—and many other bodies. Doesn't it seem wrong to burn up these useful products? And yet even now, with a great rush and hurry to build by-product ovens, fully half of the coke produced in the United States is still made in the wasteful beehive ovens. We may talk as we please about supply and demand, and reasons why and convenience, and all sorts of things, but some day we are bound to come to a clearer conception of the maxim that Waste makes Want. Some day, unless we go to pieces and lose our arts and sciences and take to the woods again like Indians, we shall have a sense of the fact that future generations have some rights, and that these precious hydrocarbons, that it has taken nature hundreds of thousands of years to produce, should not be idly destroyed as though we were a nation of drunken sailors. There is no use in growing angry or in blaming anybody for this cataclysmic waste; but now that we know better it is time to stop it.

Coke is a grand fuel and should be used more than it is. In the first place, if made in by-product coke-ovens or in gas-works, it has already been used to good purpose, so that it isn't all waste. It burns rapidly to good effect, giving heat when it is needed. Being much purer carbon than ordinary coal, it is used in industries.

Anthracite coal contains about 95 per cent. of carbon, either free or combined, and is also a good fuel in that it burns with but little ash. Ash is chiefly the mineral content of coal.

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Bituminous coal contains 80-odd per cent. of carbon, but unless it is properly fired a great waste takes place. It is also a pity to burn up the valuable hydrocarbons which it contains, and it is dirty and sooty and makes the smoke nuisance.

With the improvements that are being made in the burning of powdered coal in an air-blast it is probable that ere long most coal will be consumed in this manner. The art has been developed from the need of a very hot flame for cement manufacture, and it is already being proposed for firing boilers with considerable saving. The only thing that holds it back is that the heat is so intense that it destroys the boiler-plates. The coal must be ground just as it is fed into the boiler because in a finely powdered form coal is liable to spontaneous combustion and it is also explosive. So in burning coal powder (much finer than anthracite culm) it is blown into the fire just as it is ground. In other words, the coal-mill operates as the fire is fed. There is no smoke and no soot. The combustion is complete to  $\text{CO}_2$ . It is clean, and the full heat of the coal is developed. Now if the inventive genius of engineers is not able to meet these problems before the next generation comes along, they should be spanked and sent to bed. Think what it means: much greater efficiency of coal and no more smoke nuisance! It is bound to come, with only a few little inventions needed.

The gas-engine, in which the power is obtained by explosion within the cylinder of producer gas and air, or of gaseous hydrocarbons and air, is supplanting the steam-engine in many places. Although more expensive to build, install, and operate, and composed of more parts than the steam-engine, it is more economical in principle and already more economical in prac-

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tice in some places. Modern blast-furnace practice calls for gas-engines for the blowers.

Lignite coal contains 60 to 70 per cent. of carbon; peat, 50 to 60 per cent.; and wood, about 50 per cent.

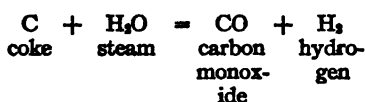
Liquid fuels are gasolene, about the lightest of the liquid petroleum bodies; kerosene, which is less volatile; crude oil; and petroleum refuse. The term fuel oil in current use indicates any petroleum product available for fuel, but it is understood to be freed from gasolene. The present value of gasolene assures this, and the expression generally represents those petroleum products for which no better market outlet may be obtained. We need not discuss them in detail; they are all hydrocarbons, and are used or not for fuel, according to the price. Alcohol is at present used as a fuel on a very small scale. Its use may increase as the art of making it from wood waste and other refuse is developed, or if better methods for denaturing it are discovered. As things are, the present laws governing the production of alcohol make the most economical manufacture impossible. It's too bad that so much may be honestly said against alcohol, which has also so many useful qualities. It burns with such a clean flame that it is the most agreeable of all fuels. The manufacture of alcohol from wood waste, such as sawdust, etc., has passed the stage of preliminary experiment and is now in operation in a limited way. The trick has been turned; it is an economical achievement.

**GASEOUS FUELS.**—Coal-gas is obtained by heating soft coal without access of air. The by-products, which are similar to those of the coke industry, are conserved, and the gas, sold for illumination and cooking, contains nearly 50 per cent. of hydrogen and

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over 40 per cent. of methane,  $\text{CH}_4$ , and about 6 per cent. of carbon monoxide. There are a great many other hydrocarbons contained in it in small amounts.

Water-gas is made by heating coke to a high temperature by blowing a blast of air over it; then steam is blown over the white-hot fuel, whereby the water is decomposed and carbon monoxide is formed, together with free hydrogen—both combustible gases:



But both of these gases burn with a blue flame, so that, to make the gas illuminating, "gas-oil" or "solar oil" from petroleum is blown in and brought to a high temperature with a view to converting the liquid hydrocarbons permanently into gases. Water-gas has less heating value than coal-gas, but it is cheaper to produce. Most large gas companies make both kinds.

**PRODUCER GAS.**—This is used chiefly for gas-engines and as a furnace fuel. It is made by passing air through incandescent coke or coal, but not in sufficient quantity to insure complete combustion and thus produce carbon dioxide,  $\text{CO}_2$ , which will not burn. Only enough air is passed through to produce carbon monoxide,  $\text{CO}$ , which, mixed with a great deal of nitrogen, is the chief constituent of producer gas. Sometimes steam is blown in with the air, decomposing the water and thus adding hydrogen and oxygen to the gas. The gas has a low heat value, but it is very cheap to produce.

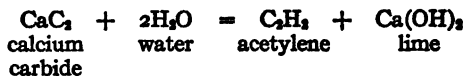
By-product gas producers provide for the recovery of the nitrogen contained in the coal by injecting

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steam into the coal-bed of the producer. The oxygen and hydrogen of the steam are torn apart by the heat, and the hydrogen combines with the nitrogen fixed in the coal to form ammonia,  $\text{NH}_3$ . Leading this into sulphuric acid produces ammonium sulphate. In England these by-product producers are largely used on low-grade or high-ash coals.

NATURAL GAS comes from the petroleum districts and is chiefly methane,  $\text{CH}_4$ . We shall discuss this gas later.

ACETYLENE,  $\text{C}_2\text{H}_2$ , is a gas of very high illuminating power now produced by the action of water upon calcium carbide,  $\text{CaC}_2$ :



It is explosive with almost any mixture of air.

Before we leave the subject of gas let us do a little prophesying. Most municipalities require gas sold to residents to have a certain candle-power in order that a lighted jet shall give not less than a designated measure of light. But since it is much more economical to burn gas in incandescent mantles which require only heat to make them glow, and no colored flame at all, there is no use in demanding a standard of candle-power. The requirement should be not twenty-two candle-power, but so many "B.T.U.," as British thermal units are called; in other words, it should produce a given amount of *heat* instead of a given amount of *light*. That would give us gas burning with a blue flame but more efficient with Welsbach mantles and for heating, and the cost of enriching it to make

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a bright light by injecting hydrocarbons would be removed. It would give us much cheaper gas and would serve instead of coal for nearly all municipal uses. It would do away with the smoke nuisance, save the by-products, and, as gas could be conveyed by pipe-lines over the country, be distributed from coke-ovens to any place where it was needed. Then the ugly factory chimneys might be torn down and the clouds of smoke and rain of soot would disappear. It is bound to come.

We are also sure to come some day to the problem of using high-ash—that is, low-grade—coals. Enormous quantities of these coals are common in the coal-fields, but nobody wants to bother with them. In by-product producers, however, they can be burned for their gas, and this used for the generation of electric power which may be transmitted considerable distances. High-ash coal does not produce good coke. The ammonia and other by-products will be saved.

Our present methods of wasting coal and befouling the air are not quite civilized in the light of present knowledge. According to the statistics of the United States Geological Survey, there were 266,204,248,000 cubic feet of artificial gas made in the United States in 1915, valued at \$173,832,132. This is an increase of 25 per cent. in quantity and 13 per cent. in value over 1912. It looks rather promising.

Treating carbon as any other element, we note that it combines with hydrogen as methane,  $\text{CH}_4$ , or marsh gas, and then in so many thousand other ways that we shall drop the subject for the present.

With oxygen it combines to  $\text{CO}$ , leaving two hooks apparently free. Carbon burned with insufficient air produces this gas. It is very poisonous and burns to produce  $\text{CO}_2$ . It unites directly with nickel



## CARBON

and iron to  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$ . Owing to its tendency to unite with oxygen to form  $\text{CO}_2$  at a high temperature, it is a good reducing agent—but only at high temperatures.

Carbon dioxide,  $\text{CO}_2$ , is the anhydrid of carbonic acid and is known as carbonic-acid gas. It is very stable, very wide-spread, and its salts with the  $\text{CO}_2$  radical we have already referred to many times. If  $\text{CO}_2$  is the anhydrid of the acid, then  $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$  would indicate the real carbonic acid. But, as we have said before, we cannot separate it in this form; it goes right over to  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Nevertheless, the salts are known. It is a very weak acid, and is easily driven off by a stronger one.  $\text{CO}_2$  is a heavy gas, and may be poured from one vessel to another in the air. It will not support combustion, and, although it is not poisonous, it will not support life. In the Dog's Grotto (Grotta del Cane) at Naples, where  $\text{CO}_2$  comes from the earth, it remains as a layer on the ground while the wind blows the upper layers of it away. If a man and a dog go into the grotto, the man passes through at his ease while the dog suffocates.

With nitrogen carbon combines (but not directly) to cyanogen,  $(\text{CN})_2$ . This  $\text{C}\equiv\text{N}$  is a gas. Far bet-



ter known is prussic acid,  $\text{HCN}$ , which is hydrogen cyanide, the most poisonous of gases, which produces cyanides of metals and forms innumerable complex salts in organic chemistry.

Of the halogen compounds we shall mention only carbon tetrachloride,  $\text{CCl}_4$ , which is a heavy liquid, over one and one-half times the weight of water, with a pungent chloroform-like odor and an anesthetic action. It is used as a solvent and for extinguishing fires.

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Carbon bisulphide,  $\text{CS}_2$ , is a volatile, highly inflammable liquid that smells like a good old orthodox idea of the Judgment Day. It is used to destroy insects, as a solvent for rubber and sulphur, and lately it has been largely used in the manufacture of artificial silk.

**PART THIRD**  
**ORGANIC CHEMISTRY**



## XIX

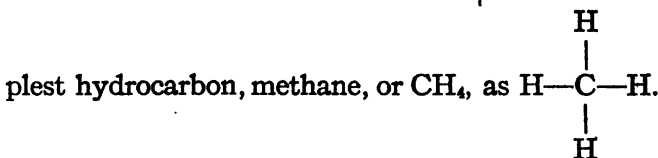
### PARAFFINS AND PETROLEUM BODIES

Paraffins, or the Fats—The Carbon Chains—Petroleum Industry—  
The Refiner's Problems—Cracking—Oil-gas—Lubricants—The  
Future of Petroleum—List of Paraffins

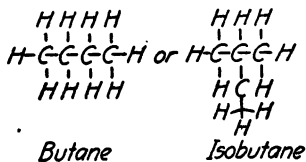
WE told in the first chapter about the manner in which one carbon atom with its four hooks will connect one or more of them with another carbon atom, leaving the free hooks to connect up with anything else that is available. We may represent the carbon atom with its four hooks as

$\begin{array}{c} | \\ -C- \\ | \end{array}$

and the simplest hydrocarbon, methane, or  $\text{CH}_4$ , as



Now let us take another body of the same methane or paraffin series, called butane, or  $\text{C}_4\text{H}_{10}$ , and we meet a new problem. The arrangement of the atoms in the molecule may be—



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and these bodies differ from one another. These are the only possible arrangements of the butane molecule. Try for yourself and see. The next body, according to the number of carbon atoms, pentane,  $C_5H_{12}$ , has three isomeric possibilities, but when we go up to, say,  $C_{12}H_{26}$ , there are 802 of these different hydrocarbons possible. We shall not pursue this agony any further except to indicate differences in fact when there is no difference in the proportionate number of carbon, hydrogen, and other atoms in the molecule. Two or more bodies having the same chemical content, but differing in the arrangement of their molecules, are called *isomers*, and their relation to one another is *isomeric*.

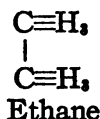
This means that molecules are real things, having shape and form and structure. Just as two different houses may be built of the same number and kind of brick and stone and yet not be at all alike, so various molecules may be constructed of the same number of C, H, and O atoms and yet be entirely different because the atoms are differently placed in their relation to one another. I pray you do not let this arouse the fear that you will not understand what follows. The subject of the respective places held by atoms in molecules is called stereochemistry, and its development is one of the great works of Jacobus Henricus van't Hoff, the great Dutch physical chemist; but we shall not enter into it. I mention it now so that we may point out certain vistas of research as we go along in considering the chemistry of living things, which is in effect the chemistry of that remarkable element carbon.

Organic compounds are generally of two great groups. The first includes the aliphatic compounds, to which all animal and vegetable fats belong. The

## PARAFFINS AND PETROLEUM BODIES

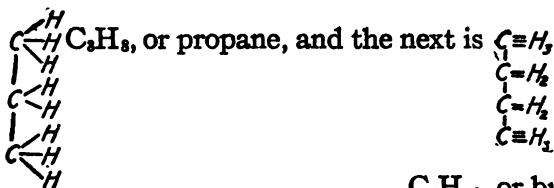
starting-point is methane,  $\text{CH}_4$ , and the first series is the paraffins, which we shall consider immediately. The second group embraces the aromatic compounds, and many of the first bodies discovered which belong to this division are characterized by an agreeable aroma. The name, however, is misleading, for some dreadful stench is produced by so-called "aromatic" bodies. The unit of the second group is benzol, or benzene,  $\text{C}_6\text{H}_6$ , which we shall consider later.

**PARAFFINS.**—One atom of carbon will combine with four atoms of hydrogen and make a stable, satisfied compound, indicated by  $\text{CH}_4$ , which is a gas and is called methane:  $\text{C}\equiv\text{H}_4$ . It is also called marsh gas, because if you stir up the bottom of a swamp, bubbles of this gas will rise. Natural gas is composed chiefly of methane. Now let us take the next in order—two atoms of carbon with all the hydrogen we can attach:



This is  $\text{C}_2\text{H}_6$ , and is called ethane.

The next would be



$\text{C}_4\text{H}_{10}$ , or butane.

The list goes up to  $\text{C}_{60}\text{H}_{122}$ , and higher.

Now let's get the anatomy of these molecules clear

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in our minds. They are, you observe, chains of carbon atoms connected with one another by a single link or bond, three hydrogen atoms at each end and two attached to each intervening carbon atom. There are twice as many hydrogen atoms as there are of carbon, and then two more, owing to the extra hydrogen atom at each end. They are composed only of carbon and hydrogen, and the general formula is  $C_nH_{2n+2}$ . These hydrocarbons are known as paraffins.

Of course, nature has what appears to be almost a passion to mix things up, and so crude petroleum has usually a great many other bodies besides this group; it contains unsatisfied hydrocarbons called olefins and that everlasting sulphur is found in combination in many oils, but this  $C_nH_{2n+2}$  is the true petroleum or paraffin group. Observe that the names end in *ane*, and after the first four, methane, ethane, propane, and butane, they take the Greek or Latin numeral corresponding to the number of carbon atoms. Thus octane is  $C_8H_{18}$ , dodecane is  $C_{12}H_{26}$ .

As the number of atoms in the molecule increases, they grow heavier and they develop from gases to light liquids, over to heavy oils, and finally to wax and pitch. This is natural; with a great mass of atoms in the molecule, the product is more likely to be solid, and with very few it tends to be gaseous. This is a truth with so many exceptions as to cast doubt upon it, but it should explain why  $CH_4$  can be a gas. As already noted, we cannot imagine a molecule of carbon to contain less than twelve carbon atoms. Diamond and graphite both surely contain a great many more.  $CH_4$ , on the other hand, contains but one, connected up with four light hydrogen atoms. No wonder it floats.

Natural gas is sometimes stripped of its heavier



## PARAFFINS AND PETROLEUM BODIES

hydrocarbons, which may be used for gasolene, while the remaining methane is sold as fuel or for light. The liquid product is known as "casing head" or natural-gas gasolene, and this brings a very good price because heavier oils may be mixed with it and the product sold as gasolene.

Crude petroleums are exceedingly variable in composition, but it is the business of the refiner to get similar marketable products from them. Or, rather, it is the business of the refiner to get out of crude bodies, oil which he can sell. The art of refining, which consists, in effect, in separating the different groups of hydrocarbons from one another by distillation, is full of difficult problems to be solved. Mr. Refiner has his crude oil as the raw product, and with his finished products he must meet the market. Formerly the great demand was for kerosene: "water white," with a fire test of  $150^{\circ}$  Fahrenheit ( $65.5^{\circ}$  centigrade), and "export oil," with a fire test of  $100^{\circ}$  Fahrenheit ( $43.3^{\circ}$  centigrade), while gasolene was a drug on the market. The difference between these bodies is that gasolene is composed of a series of hydrocarbons nearer  $\text{CH}_4$ , while kerosene is made up of a higher series, nearer the lubricating oils.

Some of us can remember when kerosene was usually dark yellow or reddish in color, and that lamp-wicks used to grow gummy. This is now avoided by treating the refined products first with sulphuric acid, which drives out of combination the tarry bodies and other undesirable products, and then treating with caustic soda takes out the remainder of that which is not wanted and also neutralizes the sulphuric acid.

The situation formerly was that the refiner could not sell his gasolene, and some of us may remember that efforts were made by the refining companies to

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develop the use of gasolene-stoves and the unwillingness of the insurance companies to insure houses and furniture where gasolene-stoves were used. The refiners wanted to get out all the kerosene and lubricating oils they could, and as little gasolene. Now the tables are turned. The amount of oil refined has increased, but not fast enough to produce enough gasolene for the increasing number of automobiles produced. On the other hand, electricity, coal-gas, and acetylene have taken the place of kerosene-oil lamps, and what with the war closing European ports, the refiners cannot sell their kerosene. Even more of a drug is the "export oil," a kerosene which flashes at a lower temperature than the United States requirements.

To meet the increased demand for gasolene, refiners have been sorely put to it. There was not enough, and there is not enough to-day. The demand is insistent. The usual test for gasolene is to measure its specific gravity—to let a hydrometer float in it. This is a glass bulb with a long graduated stem, and the specific gravity may be determined by reading the figure on the stem at the surface of the liquid and correcting the figure to accord with the temperature at the time and place. The lighter the liquid the deeper the hydrometer sinks, and *vice versa*. Now, instead of taking what they call a "single cut" of gasolene—that is, the gasolene that distills over at the required temperature—they take heavier oils and lighter ones and mix them together, thus giving the specific gravity called for, but containing bodies on both sides of gasolene as it were—heavier and lighter bodies. The chemical structure is not the same. Everything goes as gasolene until an oil is reached that is so heavy that it will carbonize in the cylinders. This is

## PARAFFINS AND PETROLEUM BODIES

not trickiness on the part of the refiners; it is grim necessity.

The heavier the petroleum bodies are the more likely they seem to be to go over into their elemental carbon and hydrogen and thus produce coke in the cylinders rather than to burn to water and carbon dioxide, the way the lighter ones do. And the presence of the heavy oils in the mixture sold as gasolene is a contributing factor to the carbonization of oils in cylinders, but it is not the sole cause. Some users mix gasolene and kerosene half and half for automobiles in summer, but cranking up a heavy car on this mixture in winter would hardly be enjoyable.

In fact, this will probably be the next step in automobile fuel—a starting device with alcohol or gasolene, and then kerosene for the trip. The tendency of kerosene to leave free carbon in the cylinders after the explosion is the greatest problem to-day, although the number of trucks using kerosene is constantly increasing. If some one will devise an improved carburetor, or if somebody else will discover an efficient oxidizing agent to mix with the kerosene so that it leaves the cylinders clean, the problem will be solved; but, despite all sorts of claims, nothing satisfactory has been brought out yet. It is likely to come soon, but whether in the carburetor or in the kerosene oxidizing agent is hard to tell.

Cracking. With the need of so much of the lighter oils, the art of “cracking” petroleum has developed. This means just what it says: the molecule is split, and lighter petroleum hydrocarbons are cracked off of it. From the residue still others may be cracked off, and in this manner the output of light hydrocarbons greatly increased, but there is a limit to this. Cracking is the general application of the rule that organic com-

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pounds are decomposed by heat. It was observed in 1855 that petroleum or its products could be distilled at other temperatures than the normal boiling-points of the constituents. What happens is, as we have just said, that parts of the molecules split off as lighter hydrocarbons, and this is termed "cracking." It is now effected by distillation under pressure or by decomposing the oil upon a highly heated surface. A process as simple as this would seem to be easy of solution, but there are tricks to it: in the first place, very heavy oils leave a residue of too much coke; some Mexican crudes, on ordinary distillation, will crack and leave a residue of 40 per cent. coke. Again, in all distillation of petroleums some cracking takes place. In cracking residues, unless the pressure is just right, the result is unsatisfactory because instead of paraffins too many unsatisfied hydrocarbons are produced which are shy of hydrogen among the lighter bodies. A little figuring will show what happens: let's take the general formula  $C_nH_{2n+2}$  and say  $n=30$ . Then we should have  $C_{30}H_{62}$ . Now if we were to split this in two we should have  $C_{15}H_{32} + C_{15}H_{30}$ , and with  $n=15$  we should have for the second body  $C_nH_{2n}$  instead of  $C_nH_{2n+2}$ . This would be an ill-smelling olefin. They do no harm, but they do not smell sweet. They may be removed by treatment with sulphuric acid. There are other reasons, however, why freshly cracked gasoline smells badly, which are: presence of sulphur compounds and traces of naphthenic acids and nitrogen bases, which are too feeble to combine. Treatment with metallic sodium or oxide of copper will cause the evil smells to disappear. It is a matter of expense. Generally speaking, the higher the pressure used in cracking the less light olefins are produced.

W. M. Burton was the first to develop the art of

## PARAFFINS AND PETROLEUM BODIES

successful cracking, and now over 3,000,000 barrels a year are produced by his process. After distilling off the gasolene and kerosene contained in the crude oil, he raises the boiling-point by back pressure upon liquid and vapors to 75 pounds per square inch in an especially arranged still.

The Rittman process consists in vaporizing the petroleum and passing it into hot tubes,  $450^{\circ}$  centigrade, under pressure of 90 to 500 pounds per square inch, according to the nature of the oil. The vapors are condensed under pressure.

An interesting chemical process which is not a cracking, but which has the same application, consists in treating the oils with  $\text{AlCl}_3$ , breaking down the high boiling oils to lower ones. A number of patents have been issued in relation to this. The advantages are that very little gas is evolved and the carbon is not deposited as hard baked on the bottom of the still, but as a granular mass, easily removed. The low-boiling oils are sweet-smelling, water white, and need no further refining.

The high-boiling oils are refined and purified, and come into use as lubricants, while still higher bodies are used for fuels. For instance, the oil that comes over after kerosene and before the lubricating oils is known as gas-oil, which is used in the manufacture of illuminating gas and was referred to under the chapter on carbon. This gas-oil, if brought to a high temperature, in an apparatus free from air, decomposes. One of the products of the decomposition is called oil-gas. Now this oil-gas, duly liquefied under pressure, is, in substance, Blaugas, which has found considerable domestic use in some localities. Oil-gas is rich in ethylene, which, upon treatment with chlorine, yields ethylene dichloride,  $\text{C}_2\text{H}_2\text{Cl}_2$ . The chlo-

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rine may be replaced by  $-OH$  groups, whereby ethylene glycol, a glycerin substitute, is obtained. It is predicted that this compound will replace glycerin for many purposes, such as the making of anti-freezing mixtures, in the treatment of leather, etc.

Lubricating oils are obtained especially from the Appalachian and mid-continent petroleums. The most important of these lubricants are so-called engine oil and cylinder stocks. The story of lubricating oils is an extremely interesting one, but too rich in detail to narrate here. Suffice it to say that where they are obtained they constitute the most valuable products of petroleum, and a great deal of skill is necessary in refining them. They range from common engine oils to those selling for several hundred dollars a gallon for lubricating watches.

### THE FUTURE OF PETROLEUM

Neither petroleum nor natural gas will last forever, especially when we consider the lavish way in which we are using up these natural products. But new uses loom up that are promising even if the present uses should be discontinued on account of cost. For instance, when the supply of natural gas wanes so that it is not economical to sell it for, say, less than fifty cents per 1,000 cubic feet, it will come into competition with power generated by gas-engines fed by by-product coke-oven gas. Then there can develop as distinct a natural-gas industry as that of coal-tar. For natural gas contains from 85 to 95 per cent. of methane,  $CH_4$ , the starting-point of the half of organic chemistry. Now let us imagine this chlorinated to carbon tetrachloride,  $CCl_4$ . Here is a solvent that needs only to be produced in this manner to find very

## PARAFFINS AND PETROLEUM BODIES

wide-spread use. The same may be said of chloroform,  $\text{CHCl}_3$ , and of dichlormethane,  $\text{CH}_2\text{Cl}_2$ , which is a better anesthetic than chloroform, and may also be used as a solvent. Methyl chloride,  $\text{CH}_3\text{Cl}$ , is a gas that will have wide application as a refrigerating agent; it boils at  $-15^\circ$  centigrade. These are industries not yet developed. Again, by oxidation, the methane may be used in the production of formic and oxalic acids, and to make formaldehyde and methyl or wood alcohol. In petroleum there are seldom found free fatty acids, but the fatty hydrocarbons are there. By treatment with chlorine and magnesium and  $\text{CO}_2$ , through a series of processes that we shall not study out, and by further treatment with sulphuric acid and water, the fatty acids are liberated, although the cost of these acids is still too high. But certain of these acids may be converted into glycerides, which mean real fats, and so, as soon as the processes are perfected, edible fats may be made from petroleum. Another subject that has already received attention is the relation of petroleum to the manufacture of soap. That would come from the artificial fatty acids produced.

Here is a list of some of the paraffin bodies with their melting-points and observed boiling-points. Note how the names after butane indicate in Latin or Greek the number of carbon atoms and how, as they increase in the number of atoms in the molecule, they are progressively liquids and then solids. This is shown in the melting-points and boiling-points.

Formula	Name	Melting-point	Observed Boiling-point
$\text{CH}_4$	Methane	$-186^\circ\text{C.}$	$-160^\circ\text{C.}$
$\text{C}_2\text{H}_6$	Ethane	$-172$	$-93$
$\text{C}_3\text{H}_8$	Propane	.....	$-45$
$\text{C}_4\text{H}_{10}$	Butane	.....	$1$

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Formula	Name	Melting-point	Observed Boiling-point
$C_5H_{12}$	Pentane	.....	36.4C.
$C_6H_{14}$	Hexane	.....	68.9
$C_7H_{16}$	Heptane	.....	98.4
$C_8H_{18}$	Octane	.....	125.6
$C_9H_{20}$	Nonane	- 51C.	149.5
$C_{10}H_{22}$	Decane	- 31	173
$C_{11}H_{24}$	Undecane	- 26	194
$C_{12}H_{26}$	Dodecane	- 12	214
$C_{14}H_{30}$	Tetradecane	4	252
$C_{16}H_{34}$	Hexadecane	18	287
$C_{20}H_{42}$	Eicosane	36.5	205
$C_{22}H_{46}$	Tricosane	47.4	234
$C_{28}H_{58}$	Pentatriacontane	74	331
$C_{30}H_{62}$	Hexacontane	101	.....

Boiling-points of eicosane, tricosane, and pentatriacontane were observed at 15 mm. pressure instead of at that of the atmosphere, which accounts for the difference.



## XX

### OLEFINS AND ACIDS

Olefins—What Unsatisfied Means in Organic Chemistry—A Little Sermon on Possibilities with Acetylene as a Text—Harmless Moving-Picture Films—Fatty Acids—Unsaturated or Unsatisfied Acids

GOING back to the paraffin bodies and bearing in mind that they are methane,  $\text{CH}_4$ ; ethane,  $\text{C}_2\text{H}_6$ ; with the general formula  $\text{C}_n\text{H}_{2n+2}$ , the olefins, as they are called, have the formula  $\text{C}_n\text{H}_{2n}$ , or two atoms less of hydrogen. The termination "ylene" is added to the type prefix, so that methylene would be  $\text{CH}_2$  and ethylene  $\text{C}_2\text{H}_4$ . They are not very stable. Methylene is not known in a free state and ethylene is a sweetish-smelling gas which combines readily with other bodies. Ethylene chloride, for instance, is  $\text{C}_2\text{H}_4\text{Cl}_2$ . You observe that the halogen adds itself on without replacing any hydrogen atoms in the molecule. They are formed in the dry distillation of complicated carbon compounds, which accounts for the presence of four to five per cent. of them in coal-gas. They are also produced by the elimination of the elements of water from alcohols and by other means as well. The lower members are gases; then, as the molecules increase in the number of atoms, they are liquids; and finally the highest members are solids. These unsaturated hydrocarbons, as they are called, are unsaturated because there are one or more carbon

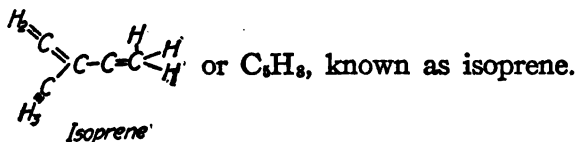
## EVERYMAN'S CHEMISTRY

bonds that are free or because the carbon atoms are hooked together by more than one bond or because carbon under certain circumstances has only two or three bonds—which looks like a fact, but is too troublesome for us to consider. The lower members of this  $C_nH_{2n}$  group are generally unstable, whereas the higher members are stable.

Another series of unsaturated hydrocarbons have the general formula  $C_nH_{2n-2}$ , which indicates that the carbon atoms are united by a triple bond, as in acetylene,  $C_2H_2$ , or  $H-C\equiv C-H$ . The second of this group,  $C_3H_4$ , is called allylene, and the higher numbers are referred to as substituted acetylenes, as  $C_4H_6$ , ethylacetylene;  $C_6H_{10}$ , butylacetylene, etc. The most important is acetylene,  $C_2H_2$ , or



It is a gas that is full of tricks. Air mixed with from 3 up to 82 per cent. of acetylene will explode. The explosive limits of air with coal-gas are only from 5 to 28 per cent. Those three bonds that are engaged in holding together the two carbon atoms are not very closely engaged. Their job is hardly enough for all three of them to keep them busy; and if anything available to combine with is around, they are likely to find it. That is where the danger from impurities in acetylene comes in. Let us indicate just one more unsaturated group in which there appear two double bonds between carbon atoms, like this:

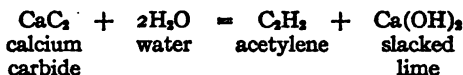


By the union of two or more molecules it passes over

## OLEFINS

with terpenes,  $C_{10}H_{16}$ , into rubber. This, then, is the road to synthetic rubber.

Acetylene, you may recall, is produced by the action of water upon calcium carbide:



Now this triple bond between the two carbon atoms,



and the fact that we have two atoms of carbon linked together, makes acetylene an interesting

starting-point for the production of many organic bodies, and whole vistas have been opened up as a result of research during the past few years. At the risk of making acetylene appear of more general importance than it is, let us consider some of the things that may be done with it. It will serve as a good example of the adventures to be met in research in organic chemistry. In other words, we started with lime and coke to make calcium carbide and by adding water we obtained acetylene. Now let us observe whither we are led from these modest beginnings, from lime and coke at the start.

Acetylene burns with a very luminous flame and is used for domestic lighting. When the carbide process was first introduced it was thought that this would be its chief use, but, while it has not achieved the popularity that was expected of it, the uses of acetylene and calcium carbide have increased in other directions, while the possibilities are illuminating as showing how unexpected the workings of organic chemistry are.

A flame of acetylene burned with oxygen is so hot

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that it will cut through several inches of iron or steel. The street-railway repair gangs are often seen using this, and it is interesting to watch them cutting through rails or welding them with the infernally hot oxyacetylene flame. It is so bright that it is dangerous to look at for any length of time, and the men need to use darkened spectacles to preserve their sight when they work with it.

Acetylene gas is compressed in cylinders by absorption in acetone and used for lighting buoys at sea, and in rivers and harbors. There are many thousand such buoys in use in the United States service. They are little lighthouses that keep going day and night for weeks at a time and need no keeper.

Another gas of the petroleum series, ethane,  $C_2H_6$ , may be produced by bringing hydrogen together with acetylene in the presence of certain metals that act as catalysts, or chemical parsons, and perform the marriage of hydrogen to acetylene, so that ethane results. There does not seem to be much call for ethane at present for chemical work, but you never can tell how soon somebody may want it in the worst way.

Now let us consider a certain German works in operation before the war. Acetylene gas under six to ten atmospheres' pressure (90 to 150 pounds to the square inch) was led into strong steel cylinders and an electric spark was passed through it. Back the whole thing went to its elemental parts of carbon and hydrogen. But this carbon was in the form of such a fine, pure soot that it was sold at handsome prices in China and Japan and to European paint manufacturers for lacquers and black varnishes.

In two other establishments, by more work with a catalyst (and this time antimony did the business),

## OLEFINS

they produced combinations with chlorine, and by that kind of chemical chicanery, which is almost more of an art than a science, a whole series of ethylene chlorides have been produced that are remarkable solvents. They are almost indifferent to metals (which means that they do not injure their containers); they are inactive toward acids and alkalies, and they do not burn easily. They are useful in the varnish, soap, and many other industries; they point to the possibility of scientific laundries in which clothes may be washed without injury, and their wide-spread use is only a matter of cost. Another of them, ethylene perchloride, is a solvent for sulphur. Then if we start with another of them, ethylene trichloride, and do various things to it, according to a Nuremberg patent, the result is—indigo! Ethylene chloride is said to be used to extract the caffeine from coffee in the Kaffee Hag works.

Beginning once more with acetylene gas and working water into the molecule, we have the aldehyde of acetic acid or acetaldehyde, and this, on oxidation, yields acetic acid. Here we have not only vinegar, but an acid greatly needed in chemical manufacture. If this were only cheap enough we should have incombustible celluloid and moving-picture films. Strangely enough, the weak acetic acid will combine with cellulose in the place of nitric acid, so that in the place of nitrocellulose or guncotton we can have acetylcellulose, which is reported to be entirely harmless. It is only a matter of cost. As soon as acetic acid is cheap enough the unburnable celluloid industry may progress. The acetaldehyde is further interesting in that by chemical strategy it is easy to make it polymerize, as the expression is, which means that its molecules may be bunched together into new combinations, and

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out of this the problem to make fatty acids is not difficult. Just how expensive it would be to make the higher fatty acids is somewhat of a guess; but from the appearance of things and the experience of men of research, it should not be very great, once the method is worked out.

Glycerin was made synthetically by Professor Friedel in Paris many years ago, but since then no one has succeeded in doing it, to my knowledge. It should be easy, but it isn't. When you think you have got it, you haven't got it at all. But you never can tell; really, you never can tell. Some day before long somebody is likely to solve it; and glycerin in simple combination with the higher fatty acids is lard, tallow, shortening, fat—what they are crying for in Germany. This is very likely to come some day, and the time may not be distant when we shall have good, pure, edible fats made from coke and lime as the starting-point.

Now if we reduce this aldehyde, behold alcohol of the old John Barleycorn type! But if, instead of doing these things, we condense acetylene under certain conditions, there results the whole string of coal-tar bodies—benzene, toluene, naphthalene, and the rest.

Again, starting with acetylene, if we mix it with ethylene, according to an Austrian patent, and then condense, chlorinate, and do other things to it, we finally get isoprene. And isoprene, on condensation, yields, as we have observed, rubber, synthetic rubber, the real gum. Butadiene, a first cousin to isoprene, is easy to make from acetylene, and the economical production of isoprene, which is most of the way to synthetic rubber, may come along any day.

Some of these processes are practical and some are not. Just now, neither indigo nor rubber may be

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profitably obtained from this source. Acetic acid, on the other hand, is made to-day in Canada in very large quantities from acetylene gas—pure, glacial acetic acid, in competition with that made from the acetate of lime of the wood distillers—and from the acetic acid they are producing acetone, which is greatly needed, among other things, for producing cordite for the British navy.

Fatty Acids. Let us go back to the paraffin bodies and negotiate a molecule of carbon dioxide into each of them. Then we shall have the fatty acid of the next higher body of the series, with the general formula  $C_nH_{2n}O_2$ . This may not be very clear, and it is not true in regard to the first of the series, but I think the idea will show itself in a minute. They are also produced by the oxidation of alcohols, but, as we have not come to alcohols yet, we can merely record it as a fact and wait awhile for the theory of it. Note, please, one other thing about organic acids, which is that they contain the group  $COOH$ , or what is

$$\begin{array}{c} O \\ || \\ -C-O-H \end{array}$$

known as the carboxyl radical,  $-C(=O)-O-H$ .

In the mean time let us consider the first of the series, or *formic acid*,  $CH_2O_2$ , or, to get it clearer,  $HCOOH$ . It is called from the Latin *formica*, which means ant, and it is, really, the unpleasant acid stuff that some ants exude in defense. It is an important acid as we shall see when we come to formaldehyde.

Of course, these acids are not produced by bubbling carbon dioxide ( $CO_2$ ) through gasolene, for instance, because the catalyst to turn the trick has not been discovered. But if we take marsh gas or methane,  $CH_4$ , and add to it, by chemical chicanery,  $CO_2$ , we have a body set forth as  $C_2H_4O_2$ , and that is

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**Acetic Acid.** Here you observe the  $\text{CO}_2$  wriggled into  $\text{CH}_4$ . This acid has been known longer than any other and is obtained by the oxidation of dilute alcohol by exposure to the air, besides the method described under acetylene. Cider, wine, beer, etc., turn sour on being left in the air, and that sour vinegar is acetic acid. This is aided by acetic-acid bacteria, called "mother" of vinegar. The absorption of O takes place only at the surface, and the process is slow. A solution of 6 to 10 per cent. acetic acid is obtained after several weeks. In the quick-vinegar process a solution of 10 per cent. alcohol is allowed to trickle over beechwood shavings in large vats through which the air circulates. The shavings are first drenched in old vinegar so as to provide some of the mother. This is a ten-day process, and the product contains 4 to 6 per cent. of acetic acid. It is also obtained by the distillation of wood. The distillate contains about 10 per cent. of acetic acid, which is caught by treatment with quicklime, so that acetate of lime is produced. This is again treated with  $\text{HCl}$ , which drives off the acetic acid, which is distilled over. It has very wide-spread use in the industries, and certain of its compounds are especially good as solvents for organic bodies. Pure acetic acid is a solid, crystalline substance which melts at  $16.6^\circ$  (about  $60^\circ$  Fahrenheit), but the addition of very little water makes it liquid.

The next in order is

**Propionic Acid**,  $\text{C}_2\text{H}_5\text{COOH}$ , or  $\text{C}_3\text{H}_6\text{O}_2$ , which we do not come across very often. Then follows

**Butyric Acid**,  $\text{C}_3\text{H}_7\text{COOH}$ , or  $\text{C}_4\text{H}_8\text{O}_2$ , which we occasionally know to our grief. It is the acid of rancid butter. It is stable and is occasionally availed of in organic research. When a chemist is compelled to work with it in the laboratory for any extended time



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his availability as a society man and dinner guest is likely to wane. It is a smell that sticks closer than a brother, and it scorns washing and rival perfumes. There are, however, some other compounds in which sulphur has taken the place of oxygen in alcohols, known as mercaptans, that can beat it. So can a number of others. In an atmosphere in which methyl or ethyl mercaptan abounds, the odor of butyric acid almost seems like precious ointment.

As we go up in the scale of these fatty acids we meet palmitic, margaric, stearic, and the higher acids, which, attached to glycerin as a base, constitute the salts or esters which are animal and vegetable fats and oils. Hence the name fatty acids. We shall observe something of their ways when we come to discuss oils. The easy rule that the more atoms there are in the molecule the more solid the product does not seem to hold good with fatty acids. Pure acetic acid is a solid at ordinary temperatures, and very much higher ones are gases.

Here is a list of some fatty acids. They may come in handy for reference some time.

Name	Formula	Melts at C.	Found in
Formic acid	H.C.O.OH	3°	Red ants.
Acetic acid	CH <sub>3</sub> COOH	16.6	Some fruit juices, especially vinegar.
Propionic acid	C <sub>2</sub> H <sub>5</sub> COOH	-36	.....
Butyric acid	C <sub>4</sub> H <sub>7</sub> COOH	-2	Rancid butter.
Valeric acid	C <sub>5</sub> H <sub>9</sub> COOH	-58.5	Valerian wood.
Capronic acid	C <sub>6</sub> H <sub>11</sub> COOH	-1.5	Rancid cocoanut oil.
Palmitic acid	C <sub>16</sub> H <sub>31</sub> COOH	62.6	As salts (esters) of
Margaric acid	C <sub>18</sub> H <sub>35</sub> COOH	60	animal and vege-
Stearic acid	C <sub>17</sub> H <sub>33</sub> COOH	69	table oils and fats.

### *Unsaturated Acids:*

Oleic Acid Series. Just for record, and because we shall have to refer to them again, let us note that

## EVERYMAN'S CHEMISTRY

these acids contain two atoms of hydrogen less than the fatty acids. Note the difference in two of them:

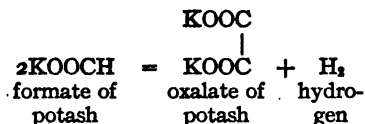
Propionic Acid (fat group) is  $C_2H_5COOH$ . Acrylic Acid (oil group) is  $C_2H_3COOH$ .

Stearic Acid (fat group) is  $C_{17}H_{35}COOH$ . Oleic Acid (oil group) is  $C_{17}H_{33}COOH$ .

These higher acids with glycerin as a base are the substance of many oils. But nature does not work according to military rules; the stearates, for instance, are not all lined up in fats and the oleates in oils. On the contrary, this base, glycerin, which we shall soon have to deal with, has three available bonds, or OH tails, and it does not mind at all having that number of different acids attached to it. The oleic group is found in fats and the fatty group in oils; all we can say is that they do not predominate. The rule is that fatty acids predominate in fats and oleic acids predominate in oils.

Oxalic Acid,  $C_2H_2O_4$ .

This belongs to a group having two COOH radicals and is the only one we shall note. Its formula is  $COOH.COOH$ , and it is prepared by fusing caustic soda and caustic potash with sawdust. This produces first a formate, which on further heating loses hydrogen and doubles up to oxalic acid, or rather, to the oxalate. Observe, please, how formic acid goes over into oxalic:



Again, oxalic acid may be switched over to formic. Oxalic acid is very poisonous, although it is often mixed with abrasives for cleaning brass and copper orna-

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ments, because it is not so corrosive as mineral acids. The other acids, malonic, succinic, etc., of this series we shall not consider, except to note that the longer the carbon chain in the molecule the weaker the acid.

## XXI

### ALCOHOLS AND SOME RELATIVES

Alcohols—List of Many Alcohols—John Barleycorn and the Drinks That Contain Him—Industrial Alcohol—Its Great Value—Glycerin—Esters and Ethers—Aldehydes and Ketones, More Especially Acetone—Halogen Compounds

LET'S go back to our original paraffins again and note that if we take out one hydrogen atom and substitute an OH—that is, an oxygen atom connected to a hydrogen atom in the place of it, we shall get the corresponding alcohol. Here is a table of a few of them:

Paraffin	Formula	Alcohol	Formula	Spec. Gr.	Boiling-point C.
Methane	CH <sub>4</sub>	Methyl, or wood	CH <sub>3</sub> OH	.812	66 <sub>0</sub>
Ethane	C <sub>2</sub> H <sub>6</sub>	Ethyl, or grain	C <sub>2</sub> H <sub>5</sub> OH	.806	78
Propane	C <sub>3</sub> H <sub>8</sub>	Propyl	C <sub>3</sub> H <sub>7</sub> OH	.817	97
Butane	C <sub>4</sub> H <sub>10</sub>	Butyl	C <sub>4</sub> H <sub>9</sub> OH	.823	117
Pentane	C <sub>5</sub> H <sub>12</sub>	Amyl, or fruit oil	C <sub>5</sub> H <sub>11</sub> OH	.829	137
Hexane	C <sub>6</sub> H <sub>14</sub>	Hexyl	C <sub>6</sub> H <sub>13</sub> OH	.833	157
Heptane	C <sub>7</sub> H <sub>16</sub>	Heptyl	C <sub>7</sub> H <sub>15</sub> OH	.836	175
Octane	C <sub>8</sub> H <sub>18</sub>	Octyl	C <sub>8</sub> H <sub>17</sub> OH	.839	191
Nonane	C <sub>9</sub> H <sub>20</sub>	Nonyl	C <sub>9</sub> H <sub>19</sub> OH	.842	213

The lowest, methyl or wood alcohol, is a very light liquid; the next, grain alcohol, is too familiar to need description. The higher bodies are oily, and as they go up the scale they become solid. By shifting that OH group around to different parts of the molecule we can get an increasing number of isomeric alcohols—

## ALCOHOLS AND SOME RELATIVES

that is, the same in content, but the atoms differently arranged in the molecule. We shall not consider them. Alcohols with five to eleven atoms of carbon are oily, and those containing more than twelve atoms of carbon are solid.

Methyl alcohol is obtained by the dry distillation of wood, keeping the air from reaching it. Three products are obtained—gases, an aqueous liquid, and tar. The liquid contains  $\frac{1}{2}$  per cent. of methyl alcohol, 10 per cent. of acetic acid, and  $\frac{1}{2}$  per cent. of acetone, more or less. The chief use of methyl alcohol is in the coal-tar color industries, as a solvent for gums and varnishes, to denature grain alcohol so that it may not be drunk, and in the production of formaldehyde.

Ethyl alcohol is old John Barleycorn. It is produced by the breaking down of sugar by means of a ferment known as yeast. We can take up the theory of this better later on, when we have considered sugars. The greatest use for alcohol still is for drinking, although it is of enormous value in industry as a solvent, in the production of varnishes, etc., in the preparation of organic bodies of all sorts, and as a disinfectant and preservative. It is said that every shell shot from a 12-inch gun represents one barrel of alcohol used in the manufacture of the powder to fire it. It ranks very high as a disinfectant. The following are the principal beverages and their alcohol content:

*Beer.* Three to 5 per cent. alcohol. Made by fermentation of malt, which is barley that has been allowed to sprout and then heated to change the starch it contains to diastase. The beer family of yeast grows on the bottom of the vat and proceeds to split the sugar into alcohol,  $C_2H_5OH$ , and carbon dioxide,  $CO_2$ . Hops are added to give flavor and to add to its keeping qualities. Very dark beer is made with

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burnt malt, and beer of the Munich type is made of pure malt and hops, while light beers are made of a mixture of malt and rice or malt and corn or a preparation of corn. Pilsener is malt and 'rice—of course, with hops added. Cheaper beers are made by substitutes, a great deal of corn for malt and producing the dark color by burnt sugar, which is caramel.

*Ale* contains from 3 to 8 per cent. of alcohol, and some stock ales contain more. The ingredients of ale are the same as beer, but the family of yeast is a different one, and the process is not the same. In ale, the yeast grows on the top of the brewing-vat and the brewing process is carried on at ordinary temperature instead of at a low one.

*Wines* are made by fermentation of the sugar in grapes. The alcohol content in dry wines is 7 to 12 per cent. Sweet wines, such as port, sherry, and madeira, contain 15 to 20 per cent. alcohol, but to produce this strength it is necessary to add alcohol because the yeast plants are killed when the alcohol content of fermenting wines reaches 17 per cent.

*Champagne* is fermented in the bottle and contains 8 to 12 per cent. alcohol.

*Whisky* contains 25 to 45 per cent. of alcohol, and is made of anything that contains sugar, but chiefly from corn (Bourbon), rye, and barley malt, and sometimes potatoes. The distiller first makes a beer and then distils over the alcohol. The "proof" of whisky is its alcohol content: 100 proof is 50 per cent.; 90 proof is 45 per cent. of alcohol, etc.

*Brandy*, with 40 to 50 per cent. of alcohol, is made by distilling wine.

*Gin* is grain liquor flavored with juniper berries and other extracts.

*Rum* is made by distilling fermented molasses.

## ALCOHOLS AND SOME RELATIVES

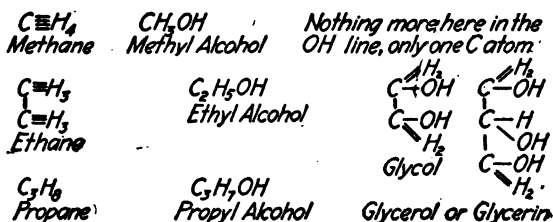
The experienced rectifier can make a great many kinds of wines and liquors with alcohol, water, sugar, and some flavoring extracts, although the wine-growers of America and the pure-food laws have brought about a better condition of alcoholic drinks than formerly obtained in this country. A vicious adulterant of whisky that was formerly sold by unscrupulous dealers was methyl or wood alcohol. It is claimed that if methyl alcohol be chemically pure it is no more poisonous than ethyl alcohol, but it is rarely made pure. The commercial product contains acetone and other impurities, and it is such a mean poison that many victims who survive a grand drunk on it lose their sight. Those whom it does not kill it is likely to blind, as it has a destructive effect upon the optic nerve and retina. The demand for methyl alcohol has increased the price and the pure-food laws have discouraged the practice. Most of the ethyl alcohol made for industrial use is produced by the fermentation of molasses, after which the spirit is distilled off and cooled. It is denatured by adding to it ill-smelling substances that make it unfit to drink. Pyridine ( $C_5H_5N$ ), which smells like stale tobacco-smoke with remorse added to it, is often used for this purpose. We have never heard of any one with a craving for it. The United States Treasury Department provides a long list of denaturing agents to meet the different industrial uses to which the alcohol is to be put. It has already come into considerable use for cooking-stoves and for lighting with Welsbach mantles.

### GLYCOL AND GLYCERIN

We have observed how, by substituting OH for H in a paraffin, we get an alcohol. Now among the vari-

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ous idiosyncrasies of carbon is the fact that it does not like to have more than one OH group attached to one carbon atom. You may, by chemical strategy, succeed in getting a second OH attached to it, but it will not stay, and time and again, when you think you are likely to succeed, the whole thing will play a trick on you and break down into something entirely different. But we have those alcohols with one OH, and they act something like an alkali; they produce salts, or esters, as they are called in organic chemistry, with acids. We do not need to put more than one OH group upon one carbon atom; there is plenty of room for more. So let us add several OH groups and see what happens:



Here we have something sweet and sticky and that acts in a mild way as a base. Glycol is a dihydric alcohol, and glycerin is a trihydric alcohol. In the place of each of those OH groups an acid radical can take its place, and this is the great base of oils and fats that we find in nature. It is this one particular body,  $\text{C}_3\text{H}_5\text{O}_3$ , glycerol, or glycerin, as it is more popularly called, that we find in all fats and oils, instead of a whole series running up and down the list. We shall meet its cousins of many atoms when we come to sugars, but for the present we are busy with nature's great organic base. It is sweet and sticky



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and very hygroscopic or deliquescent, which means that it has a grand thirst for water. Fats and oils that are esters or salts of glycerin with organic acids are also called glycerides. Boil up a fat with a caustic alkali, such as caustic soda, and you produce soap and glycerin.

Aside from its use in medicine, chiefly as an emollient, and in chemical industry, in dyeing and printing, and for anti-freezing compounds, its greatest use is in nitroglycerin for explosives. In the place of each of those three OH groups, nitric acid may hook itself on and we may have mono-, di-, or tri-nitroglycerin. For explosives the trinitrate is employed, and the formula is  $C_3H_5(NO_3)_3$ . It is a heavy, oily liquid having a sickly odor, and after it is carefully washed and brought to a pure state it does not explode spontaneously. Mixed with infusorial earth, which is in effect very finely divided particles of silicon dioxide,  $SiO_2$ , it forms a soft, plastic mass which can be molded in the hands. This dynamite is about 25 per cent. infusorial earth and 75 per cent. nitroglycerin. This was Alfred Nobel's original dynamite; now many different mixtures are made, including oxidizing agents and nitrocellulose.

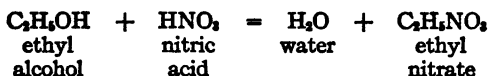
## ESTERS AND ETHERS

If an acid with its hydrogen ion meets a base with its OH ion in inorganic chemistry, a salt is formed, and the H of the acid and the OH of the base combine to produce  $H_2O$ , or water. In organic chemistry the process is much slower; the OH groups of the alcohols and other bodies which contain them do unite with the H of the acids to produce water,  $H_2O$ , while the rest of the acid and the alcohol, glycerol, or whatever it may

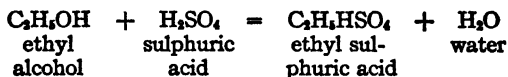
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be, slowly combine into what is called an ester. Ester is the expression for salt in organic chemistry. Whether this name came from the Bible or not is more than I can say, except that some of the esters are fragrant and have strong fruity odors. Many perfumes, whether natural or artificial, are complex ethers and esters. And Esther of Holy Writ, you may recall, was purified, "to wit, six months with oil of myrrh and six months with sweet odors and with other things," but just how pious the first man was who called these salts esters we do not know.

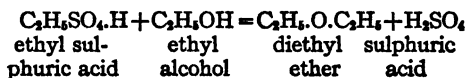
There are also esters of inorganic acids. Thus if we bring alcohol and nitric acid together we have an ester.



*Ethers.* If we take two molecules of an alcohol, and then from the two take one molecule of water, leaving one atom of oxygen as a kind of hinge to connect them together, we have an ether. Let us do that in two operations:



Now let us add more alcohol, and we have



Observe, please, that you get the sulphuric acid back again, so that a little of it goes a long way in making ether.

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The number of possible ethers is twice as many as there are alcohols, because two different alcohols may be connected up by an oxygen atom. The above, diethyl ether, is the one best known and is used in the production of anesthesia.

### ALDEHYDES AND KETONES

If we take two atoms of hydrogen from an alcohol we get what is called the corresponding aldehyde, and if we add an atom of oxygen to the aldehyde we get the corresponding acid. The name aldehyde indicates dehydrogenated alcohol, or *al*(cohol) *dehyd*(rogenatus), and that which is best known is formaldehyde, the first of the series, corresponding to formic acid, which in turn corresponds to the methane group. Methyl alcohol is  $\text{CH}_3\text{OH}$ , formaldehyde is  $\text{CH}_2\text{O}$ , formic acid is  $\text{CHOOH}$ . Ethyl alcohol is  $\text{C}_2\text{H}_5\text{OH}$ , ethyl aldehyde is  $\text{C}_2\text{H}_3\text{OH}$ , and acetic acid is  $\text{C}_2\text{H}_3\text{O.OH}$ .

Formaldehyde is a gas, soluble in water, and everybody knows its unpleasant smell. It is an excellent antiseptic and an active poison. It is produced from wood alcohol (methyl alcohol). It has the trick of polymerizing, as it is called—that is, of multiplying up its molecules into other bodies by doubling, tripling, quadrupling, etc., until molecules of a very high number of atoms are obtained. If brought into contact with carbolic acid, it forms a precipitate, and when this precipitate is heated and pressed under just the right conditions the well-known substance Bakelite and other similar products are made. The method is just the one you would expect. Here we have a body, which by heating, to loosen up the hooks of the atoms in the molecule and by pressing at the same

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time, we get new molecules with much larger numbers of atoms in them. The higher series are gums, and Bakelite in its final form is one of the most inert substances known in regard to acids, alkalies, and electricity. It looks like amber, but can be colored and made opaque; it is very largely used in electrical apparatus; it makes excellent billiard-balls, being somewhat livelier than ivory, and is used for pipe-stems and all other things for which amber is employed.

Ketones have the same general formula as the aldehydes, but the arrangement of the atoms in the molecule is different. Acetone, the first of the series, and the most popularly known, is represented by  $\text{CH}_3\text{-CO}\cdot\text{CH}_3$ . It is, you observe, a methyl group on either side of a CO group. There is one free hook to each of the  $\text{CH}_3$  radicals, and there are two left over from the CO group of atoms. Acetone is prepared from acetate of lime and is used in chemical industry. It is miscible with water in all proportions, and is especially valuable as a solvent. Acetate of lime, you may recall, is a product of the distillation of wood. A new method of producing acetone is by means of a yeast which ferments sugar into acetone, hydrogen, and other bodies. Over half of the world's production of acetone is made in one works from acetic acid, which, in turn, is obtained from the oxidation of ethyl alcohol. Great quantities are needed in the manufacture of cordite.

As might be expected, the halogens take the place of hydrogen in these hydrocarbons, according to their nature. Fluorine is very energetic, chlorine less so, and iodine will not react directly with them, but requires a little chemical coaxing to bring it into combination. We shall mention only a few of these products.

Chloroform is methane,  $\text{CH}_4$ , with three hydrogen

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atoms substituted by chlorine to  $\text{CHCl}_3$ . It is not a very stable liquid, decomposing under the influence of light and air, and is always preserved by ethyl alcohol. Its use is chiefly as an anesthetic, but it has also valuable solvent properties.

Carbon tetrachloride we have already described, and iodoform,  $\text{CHI}_3$ , is a yellow crystalline substance used in surgery as an antiseptic.

## XXII

### FATS, OILS, AND THEIR PRODUCTS

How Nature Sometimes Makes a Mistake—Need of Fats—A General  
Petition for Cleanliness—Refining Oils—List of Well-known Oils  
—Hardening Oils—Theory and Practice—Oleomargarine—Nothing  
to Be Afraid of—Soap—Theory—Practice—Twitchell Process  
—Toilet Soaps—Washing Clothes—Improvements

WE have discussed at some length the various fatty acids and we have also considered the base of fats and oils, which is glycerin. Nature has a way of storing up energy in fats. They have a high value in producing body heat and body energy, and they form layers of protective tissue which serve as storehouses to be drawn on in emergencies. Of course, nature does not always get just the right information and sometimes proceeds to provide layer upon layer of fat where it is neither wanted nor needed. Metabolism is an odd series of processes, and we do not of necessity grow fat by eating glycerides. On the other hand, fatty degeneration may set in at any time, and the most abstemious and athletic man may puff up like a porker for no reason that can be ascertained, or, at all events, for no reason that will satisfy him. There is also a legend to the effect that ladies sometimes grow weary of the increasing abundance of their charm.

In this chapter, however, we are not discussing human fat, but rather that of lower animals which is

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sold as lard or tallow, and the fats of plants, or rather seeds, which are usually oils. Both lard and tallow are chiefly stearates of glycerin and the principal observation that has been made concerning them during the past few years is that there is not enough to go round; hence the rise in price. We must have fats, however, and fortunately a way has been discovered to give us all the hard fats we need through the hydrogenation of oils. We should remember that these oils, whether from plants or animals, are very similar in constitution and that they need good treatment, especially if they are to be hardened into fats for eating. We do not let a hog lie around after it has been slaughtered before the lard is removed, and no more should vegetable oils be allowed to degenerate before they are refined. Oils must be fresh and the speed of refining as well as the methods by which they are obtained are great factors in their quality.

A large amount of palm and cocoanut oil comes from the tropics in very bad condition, although of late efforts have been made to improve conditions under civilized control. But reforms are slow in coming about. Not long ago some oil-presses were sent to the tropics to press out palm and cocoanut oils, and word came back that "the presses were too heavy for women and children to operate." Millions of dollars would be saved annually in the United States alone if oils were properly instead of carelessly rendered. Peanut oil, for instance, made of Algerian peanuts and pressed in France, comes in splendid shape. Domestic peanuts, at the present writing, are often not even husked before pressing, and they are frequently pressed in cotton-seed oil-presses that have not even been cleaned before the operation. Let us hope that this defect may soon be corrected.

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Cotton-seed oil has the habit of growing rancid in the seed if the weather is wet; therefore the cotton-oil crop is always poor after a wet season. Corn-oil, which contains a considerable amount of unsaponifiable matter, is usually handled in a clean manner and it is growing in favor as an edible oil.

In refining oils it is preferable to employ physical methods rather than chemical reagents, because oils are so delicate and complex that it is easy to tear them to pieces, constitutionally, with acids and alkalis. There are, however, nearly always some free fatty acids in oils, and these increase as time goes on. To avoid this increase it is necessary to add a slight amount of alkali to neutralize them in refining. This, of course, produces soap, which is precipitated usually with clay.

After oil is pressed from nuts or seed it should be allowed to settle immediately and the pulp and albuminous matter precipitated with clay. Pulp is vexatious stuff in oils; it darkens them and makes them rancid. The color and turbidity are removed by fullers' earth, and the odor, except that of fullers' earth, is removed by passing through charcoal. The earthy taste and smell are blown out by steam. Some oils are bleached and their pigments oxidized by blowing air through them. Linseed and soya-bean oils are bleached by heating up to 200° centigrade, whereby the pigments are carbonized and the color grows light.

An interesting process is that discovered and patented by Prof. Charles Baskerville, of New York, which provides for immediate refining of oils after pressing—a great desideratum. The oils, after pressing, are run into a settling-tank and there treated with cellulose, usually in the form of wood-pulp, and a slight amount of soda. The pulp absorbs the coloring-



## FATS, OILS, AND THEIR PRODUCTS

matter and other impurities, together with the soap produced by the soda, and is separated from the oil by filter presses.

The following are some of the principal oils that come upon the markets of the United States:

Lard and Tallow Oils. Almost entirely used in the production of artificial butter.

Cotton-seed. The old stand-by. The largest use is for foods. The next single use is to make "pure Castile soap from olive-oil. The olives from the Mount of Olives." Marseilles, France, is the headquarters for Castile soap, and the French use chiefly cotton-seed, peanut, and sesame oils for their product. It is hardened into "Crisco" and similar products, and Doctor Wesson has succeeded in refining it into a very good salad-oil.

The Olive is needed in certain industries as well as for salads and cooking. The Latin and Mediterranean peoples cook with oil, the Teutonic and Slavic peoples with hard fats. The line is as clearly drawn as is the line of language which divides the races.

The Soya-bean is a very important oil. It comes from China and Indo-China, although it could also be grown in many parts of the United States. It is edible, is good soap stock, and it is said to have fair drying qualities. There appears to be a great future for the soya bean.

Peanut is a good substitute for cotton-seed oil and should have a good future. It is edible, hardens well, and is good soap stock.

Fish-oil is sometimes used in cheap mixed paints; it hardens well and loses its odor in the process, provided it is thoroughly done.

Castor-oil is a medicine, a lubricant, and used in the dyeing industry as Turkey-red oil.

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Cocoanut-oil has advantages in soap-making. It contains some low, fatty acids, of which the sodium esters, or soaps, are somewhat soluble in hard and salt water. This makes cocoanut-oil soaps available over a wide range.

Cocoa butter is that which is pressed from the chocolate bean and is the most expensive of the fats mentioned. It is used in the manufacture of confectionery and for toilet preparations.

Chinese vegetable tallow is an odd fat which usually comes here in rather bad shape. It is a good soap stock, but it has an odd peculiarity that may make it a great convenience to some inventor who wants just this quality. Like water and antimony, it *expands as it hardens*, so that if it is melted and poured into a glass or earthenware vessel of any kind it will break the vessel as it hardens. It is hard at ordinary temperatures. The peculiarity of hardening as it expands would make it valuable in taking the exact shape of strong molds, just as antimony causes type metal to take the complete form in the matrix.

Hardening oils, or hydrogenation of fats, as it is called, is one of the noteworthy accomplishments of modern industrial chemistry. As a research achievement it ranks in importance with the cracking of petroleum to produce gasoline and with the flotation process for concentrating ores.

Let us recall what we observed of the comparison between fatty acids and those of the oleic group and note that their only difference is that of two atoms of hydrogen. For instance:

Propionic Acid (fatty group) is  $C_2H_5.COOH$ .  
Acrylic Acid (oleic group) is  $C_2H_3.COOH$ .

Stearic Acid (fatty group) is  $C_{17}H_{35}COOH$ . Oleic Acid (oleic group) is  $C_{17}H_{33}COOH$ .

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Now there are other acids found in fats and oils, but chiefly in oils, and some contain four atoms of hydrogen less than the corresponding fatty acid. Linoleic acid (from linseed-oil) is six hydrogen atoms shy, and among fish-oils there is one acid that has eight hydrogen atoms less than the fatty acid with the same number of carbon atoms. Linseed and fish oils have drying qualities, which may be due to these unsaturated bodies, but linseed-oil is far better.

If, then, in the hard fats the most of the acids are like stearic, which has all the hydrogen it can carry—and most of the acids in the oils have not as much hydrogen as they can carry—it follows that if we can intrigue a couple or more of hydrogen atoms into the molecules of these oils, getting them into their right places, we shall shift the series over from the unsatisfied oleic and lower groups into fatty acids. In other words, if the only difference between stearic or fat acid and oleic or oil acid is hydrogen, then if we put the hydrogen in we shall change the oil to a fat. The glycerin is not interested in the operation; it is just as well satisfied if mated to the one as it is to the other. Indeed, it is often combined, as we have said, with two or even three different acids at each of its available places. Getting the necessary hydrogen atoms into the oil molecules is the trick we should like to turn, although we can let hydrogen gas bubble through cotton-seed or palm or soya-bean or olive or peanut or any other oil to our heart's content, and nothing will happen. But here comes the catalyst: some *very* finely divided nickel, for instance, or platinum or palladium (both of which are too expensive) will introduce the H atoms. These are led into the oil into just the place where they are needed, along with the hydrogen, and up comes your oil as nice, clean,

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white fat. It is fat, stearic, palmitic, etc., glycerol esters.

When we consider the rate at which meats, including their fats, have increased in cost of late years and the increase of the population of cities, always calling for more meat and more fat, we can appreciate the value of this invention, which will turn nearly any good, pure, non-poisonous oil into edible fat—substantially into lard.

So far, nickel has proved to be the great catalyst for this purpose, and the reason why it must be very finely divided is that it appears that the H will go into combination only when the particles of Ni, oil, and H are all three in contact. Another excellent reason is that it will not work unless the Ni is very finely divided, finer than we can grind it. So it is precipitated out of a nickel salt in a condition fine enough to do the work. An interesting feature is that the nickel apparently gets tired and refuses to work after a while. Then it must be heated to drive off the oil, whereby it also becomes oxidized. Next it is heated again in a current of hydrogen and thus reduced. Then it is ready for business as before.

After the operation of hardening oils is over there is some nickel that remains in the fat, and it is so finely divided that it cannot be removed. But this need not worry us. There is less nickel in these fats than is obtained by cooking in a nickel-plated chafing-dish. It is estimated that not over six parts of nickel remain in 10,000,000 parts of fat.

Hydrogen is very slightly soluble in oils, so that a general agitation or mixing up is necessary to bring about the triple contact. Pressure also speeds up the reaction, but it is hard to keep the hydrogen in the autoclaves under pressure. To make an autoclave or

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pressure vessel with an agitator air-tight is quite a task; the attempt to make it hydrogen-tight is more than likely to involve unprofitable and unsuccessful profanity.

The modern method is to attach the nickel to some light, inert substance to keep it afloat, and this aids in effecting the triple contact. A fairly high temperature is necessary— $180^{\circ}$  to  $190^{\circ}$  centigrade is best. At  $100^{\circ}$  centigrade the operation proceeds very slowly. There are a great many patents covering various processes in the art, and at the present writing opposing interests are engaged in trial at law to determine their rights and privileges.

Hydrogenation may be stopped at any stage, and very hard fats may be mixed with untreated oils so that any degree of hardness or softness may be obtained. The principal use of hardened oils is for cooking and for use in soaps. Soya-bean, peanut, and corn oils are coming into favor as edible products along with cotton-seed oil.

**OLEOMARGARINE.**—Three kinds of this artificial butter are produced:

1. White;
2. Tinted (natural color);
3. Colored (artificially).

The best is the white, made from the best beef fat, neutral lard, with some cotton-seed or peanut oil. The tinted includes some of the yellower oleo oils, while the colored is colored with annatto, a coloring-matter obtained from the seed petals of the annatto tree of South America. The ingredients are similar to those of the white.

The so-called oleo oils are the oils of lard and tallow. They are expressed in the lard refineries and then

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beaten up or emulsified with milk. It is very important that a good, rich grade of milk be used which is first pasteurized and then allowed to "ripen" or grow sour, just as sour cream is used for butter. The oils are heated and the fats melted under carefully regulated temperatures, then weighed off and run into the churn or emulsifier, which contains ripened milk. The churning lasts from fifteen minutes to an hour, and then the whole is run into a tank under a spray of ice-water, whereupon the butter floats on the ice-water and milk and is skimmed off. These tanks are called crystallizing tanks. The butter is left some time in containers to drain and to take on the flavor of the milk that is left in it. Then it is worked like real butter, salted, and packed for sale.

The process as carried on in large factories is a clean one, and as the fats are practically sterilized and the milk pasteurized, oleomargarine does not carry the hazard of the bacilli of disease that may be found in defective but genuine butter.

Unsalted oleomargarine has very little taste and is not so good a substitute for fresh or unsalted butter as it is for that which is salted. The differences in taste are greater.

Oleomargarine yield nearly twice the amount of food principle computed in calories compared with that provided by butter, although butter fat also carries minute peculiar bodies which some maintain are needed in animal metabolism. Some manufacturers provide along with the best white oleomargarine little tubes of annatto, so that the thrifty housewife may color her artificial butter as she desires it. The tax on the white and tinted product in the United States is one-fourth of a cent per pound; the tax on the colored oleomargarine is ten cents per pound. There was pro-

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duced in the United States from April 1, 1915, to April 1, 1916, 147,156,197 pounds of oleomargarine.

SOAP.—Fats, as we know them, whether liquid, as olive or cotton-seed oil, or solid, as beef suet, you will remember, are esters or salts of the higher fatty or oleic acids with glycerin. When these are boiled with an alkali such as caustic soda, we get the sodium salts or esters of the fatty acids, *and that is soap*. Any strong alkali will produce a soap, and the process of splitting a fat into its acid parts and glycerin is called saponification. The by-product is glycerin. Potash soap is soft; sodium soap is hard, and that is the product that we use every day.

What happens, then, when we wash our hands and get rid of the dirt with the soap? In the first place, a certain amount of our own fat oozes out through the skin constantly, through the sweat-glands—not through the pores, as many believe. This fatty sweat is sticky, and holds the dirt on. Now soap, being a salt of a metallic alkali with a high fatty acid, is not a very robust compound; the base is strong, but the acid is weak. When dissolved in water it dissociates in part to free acid and free alkali. If we add more water to the solution, more free stearic or palmitic or whatever the acids may be are freed, as is more alkali, but the additional water keeps it in dilution, so that we never get very much free alkali from a good soap. The free acid combines with another molecule of soap and produces a light, insoluble compound, which is suds. The suds act as a mechanical carrier and carry away the particles of dirt which have been liberated by the just-enough-but-not-too-much free alkali. The free alkali attacks the grease it finds and makes more soap of it. That is the theory, or

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at least a theory, which seems reasonable. Others maintain that soap acts as a cleaner because of its lubricating and solvent power. Let us not dispute over it.

Caustic soda or sodium carbonate would do just as well so far as loosening up the dirt is concerned. The trouble is we should get the alkaline solution too strong and injure the skin or the cloth. The great merit of soap, so far as its free alkali is concerned, is its moderation, its temperance. Then the lather is a great convenience.

When soap is made by boiling up fats with caustic soda the product is driven out of solution by adding salt. Then the soap floats on top in flakes and the glycerin and salt water are below. When the soap is pressed out it sinks, but it can be made to float by blowing air into it.

Now you may recall why hard water is undesirable for use with soap. We explained how the lime and magnesia that it contains change place with the sodium in the esters of the fatty acids and produce lime and magnesia soaps which are insoluble, while we were discussing water.

An improved method of saponification or the splitting of fats is the process of Dr. Ernest Twitchell, of Cincinnati. He provides a catalyst (a "saponifier," he calls it), consisting of a fatty acid coupled up with naphthalene, and this is further treated with sulphuric acid, so that a fatty, aromatic, sulphonc acid is produced. A very little of this— $\frac{1}{2}$  of 1 per cent. of the weight of the fat—will effectively split the entire batch. The glycerin then contains no salt and very few other impurities, while the fatty acids, even if produced from low-grade fats, may be purified by distillation. Soap is then made by bringing the acids into



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contact with soda ash instead of the more expensive caustic soda that is used in the old method. The Twitchell process is in large use by progressive manufacturers.

Soap is soap—softer if made with potash and harder if made with soda. Roughly speaking, cheap soaps are likely to be made of vegetable fats to a greater extent than expensive products, and yet very often the big, yellow cakes of the laundry and the scented Thing of Perfection in the boudoir are made from the same stock. Many French persons always use American soaps on the ground that they are the best. Many Americans, on the other hand, prefer French soaps for toilet use on the ground that they are still better. Others buy whichever costs the most in the same search after perfection. Now soap, I repeat, is soap, and the things you pay for in fancy soaps are things to please—perfume, rosin, filler, and emollients of one sort or another, not forgetting the wrapper. It is not chemistry that makes a piece of good, neutral soap with no free alkali a little scented nubbins worth fifty cents; it is art.

*Washing clothes* or laundering is an art that has not changed in any major way for many years. There are the clothes and the dirt on the one hand and soap and water on the other, and the best we know how to do is to rub them all together, rinse them out, and dry them. Then after they are bleached, starched, and ironed, they are ready for use again. There's nothing new in this. But in minor details there have been many changes, and it is fair to say that greater improvements have been made in the public laundries than in the laundry of the household.

The general practice in commercial laundries is first to check and mark the goods. Fine linens that may

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not be marked up are put into nets and each net bears a tag. Then the wash is made up into lots and these lots go through the whole process as single batches. Each lot then is first put through the wheel in cold water, soap, and soda. To about 240 pounds of water (30 gallons)  $\frac{1}{2}$  pound of soda and 1 pound of soap are used. These amounts vary according to the hardness of the water and the condition of the clothes. The entire process in the wheel, which is constantly in motion, lasts about half an hour, but the cold water bath is over in fifteen minutes. The object of the cold bath is to remove the albumen which coagulates and hardens in the heat. This water is discharged and the clothes are rinsed. Then follows a run in hot water and soap, 150 to 180° Fahrenheit (65-80° C.), enough soap being used to make a good suds. Here again we observe the need of using soft water, because whatever measure of hardness there is in the water will destroy the corresponding amount of soap by making it insoluble. If the run is on collars and shirts, a little bleach, preferably hypochlorite of soda, is put in about ten minutes before the end. The goods then receive three successive rinses, about five minutes each, and then comes the blue solution, usually aniline blue and sometimes ultramarine, lukewarm, for about ten minutes. There is likely to remain a little alkali at this time which tends to give the clothes a grayish tinge, which is overcome by a little acetic or oxalic acid, which the laundryman calls his "sour." This neutralizes the alkali and brings out the blue. Then follow two or three rinsings in warm or cold water and the whole lot is put into the centrifuge.

Starched goods are dried and dampened before ironing, while underwear and such goods as should

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be very soft and flexible are dried in a rotary dryer with hot air passing through.

Home washing has the advantage that the clothes receive selective treatment; goods are washed until they are clean and no longer.

Commercial laundries make some selection between the very dirty and the moderately dirty goods, but the selection is not exact. Whatever is put into a lot goes through with the lot, whether it needs so much washing or not. On the other hand, the laundry wheel does not give clothes such rough treatment as a washing-board. Scientific laundrymen are much more conscientious as to the materials they use than is the casual laundress.

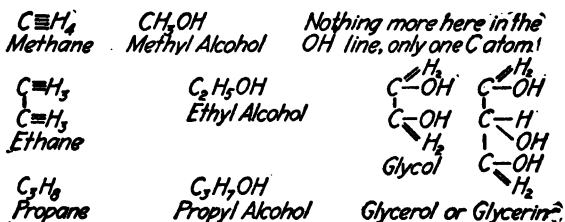
The improvements made in the art of washing clothes and cloth as the result of chemical research, especially at the Mellon Institute of the University of Pittsburgh, have done away in good laundries with the practice of using lye and bleaching-powder, have reduced the amount of bleach and acid used in very large measure, and the present work is toward discovering the real action of soap solutions and their effects upon fibers, the action of plain water and of mechanical processes. When the best results are discovered the methods will be standardized. Many foolish preparations sold under fancy names and labels at high prices have been analyzed and proved to be mere catchpenny devices.

## XXIII

### SUGARS, STARCH AND GUMS

The Steps from Paraffins to Sugars—The Many Different Sugars—The Study of Them—Emil Fischer and Van't Hoff—Making Cane or Beet Sugar—Sucrose and Glucose—Candy—Chewing-gum—Gums and Varnishes—Varnishes and Paints—A World Full of Troubles

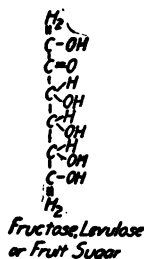
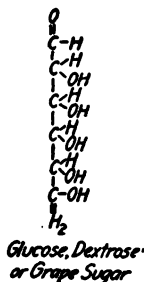
LET us go back to the paraffins and recall those chains of hydrocarbons in which the carbon atoms are linked together by one bond, and the other affinities satisfied with hydrogen. Methane,  $\text{CH}_4$ , is the first of the series; ethane,  $\text{C}_2\text{H}_6$ , is the next; and so on. Then the alcohols are produced by the substitution of an OH group for a hydrogen atom, and you may remember that a carbon atom does not like to carry more than one OH group. Then, recalling the note on glycerin, let us repeat the formula given to explain it:



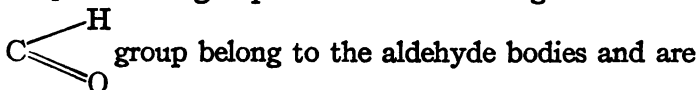
In other words, as we fill up the places of hydrogen with OH radicals we get compounds that are sweet

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and sticky. Now let us make longer chains and we have:



Roughly speaking, then, a sugar is an aliphatic chain having many OH radicals and one or more  $\text{CH}_2\text{OH}$  or CO groups in the molecule. Sugars with the



called aldoses. Those with the CO group, on account of their relation to ketones, are called ketoses. Such are all simple sugars. "Ose" is the termination of the chemical names of all sugars. A simple sugar is a sugar of one chain of carbon atoms, and they are called monosaccharides. Now let us imagine two simple sugars joined together with the loss of water ( $\text{H}_2\text{O}$ ), which is called dehydration, and then we should have a sugar composed of two chains, which would be called a disaccharide. Here we are getting back to familiar ground again, for sucrose is none other than cane or beet sugar, the sugar of the household, the substance of the lump that goes into the cup of coffee. Observe, then, please, that *sucrose* is a disaccharide composed of glucose and fructose, less one molecule of water.

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*Maltose* is a disaccharide composed of two glucose molecules joined.

*Milk sugar* is a disaccharide composed of glucose and galactose, all, of course, less one molecule of water.

Now if we join three simple sugars together we have trisaccharides. Thus, raffinose, an impurity of cane-sugar, is a trisaccharide. Just as the lower members are not exactly sugars, but rather glycol and glycerol or glycerin, so the higher members beyond which these chains of glucose, fructose, etc., are combined as polysaccharides, many in one molecule, cease to be sugars but get to be starches and gums. And further on, with still more chains of these simple sugars all polymerized into molecules as big as your fist, if you undertake to write them down and really know their constitution, and your writing is not too fine, we have cellulose! *That* is the reason why alcohol may be made from sawdust. The whole list is known as carbohydrates.

It would seem, then, that it would be an easy task to make any sugar we want; that if we have glucose and fructose we could "just take and go to work" and dehydrate them and there we should have all the table sugar we want made out of corn and pumpkins. But here we come to a difficulty again. By the action of acids the polysaccharides are easily broken up into simple sugars; that is easy and is the basis of the glucose industry. But the other way about, the locking up of simple sugars into the more complex bodies, is a trick that nature knows but that we haven't learned yet. All of these carbohydrates are made by nature out of carbon dioxide and water—sugars, starches, gums, and cellulose. Two monosaccharides have been dehydrated to a disaccharide, but only with

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great pains and circumstance. And even then it did not turn out as it was expected to.

The history of the study of sugars is interesting. They are all sweet and soluble and gummy. Both acids and alkalies break them down so effectively that their structure is lost in the operation, and so the work on sugars was formerly very indefinite. Then the problem was to get some crystalline derivative of the sugars that was distinctly marked in each case. In 1887 Emil Fischer discovered this: he found that phenylhydrazine in the presence of acetic acid makes with sugars beautiful, moderately soluble crystals which are called osazones, that every sugar has its own distinct characteristics, and that by this means the different sugars may be recognized. Just consider the patience it must have taken to discover this! He had been working for years on the subject.

But that was not enough. The osazones showed that there were a great many kinds of sugars, but what were they? The proportions of carbon, hydrogen, and oxygen in the molecule are the same in many different kinds—the many isomeric sugars that are the same in composition and yet different in the relative positions occupied by the atoms within the molecules. So we must consider the work of Jacobus Henricus van't Hoff, a young Dutch chemist from Delft. He studied in Paris and in Bonn. As a student he was more of a dreamer than a chemist; he had a philosophical turn of mind and a head for mathematics. His avocation was the study of Byron, and he caused somewhat of a flutter in the dove-cotes by writing very pretty poems in English to the attractive girls that he met. When he came to Bonn, where Professor Kekulé at that time was teaching, and had worked out the formula for the benzol ring, he

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was curious to know where those carbon bonds were. If that benzol molecule was a thing, what shape was it? If there were those four bonds attached to each carbon atom, which way did they reach out? That an atom is almost infinitely small did not disturb his mathematical mind in the least. The great Kekulé did not help him, neither did anybody else, so he proceeded to work out the study of stereochemistry, or place-chemistry, which, as we have said, we shall not develop in this work. Suffice it to say that van't Hoff worked out his theories and published them against angry and scornful opposition. He had returned to Holland by this time and was lecturing in a veterinary college in Amsterdam, and "the Dutch horse-doctor" was assured that he was an ignoramus and everything else undesirable. But van't Hoff bided his time. He had faith. Finally the great Emil Fischer applied the work of van't Hoff to his sugars. He found, according to stereochemistry, that there were sixteen different kinds of glucose possible. By 1893 he had made eleven of them, and now they have all been produced. Without stereochemistry the knowledge of these things would have been impossible. Since then the study of sugars has been carried on by Nef and others, and the subject constitutes one of the most thoroughly studied branches of organic chemistry.

Cane-sugar, or sucrose, is found in sugar-cane, in beets, sorghum, sugar-maple sap, and honey. At one time great hopes were entertained of making sugar from sorghum, but the beet-sugar industry has taken its place. The tropical sugar-cane is harvested and the cane is cut or lacerated, and then run through heavy rollers to squeeze out the juice. The beets are cut into long, thin slices in order to break up the



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membranes of the cells which contain the sugar. These are placed in vats through which water circulates, the nearly exhausted material being acted on by fresh water while the material richest in sugar is treated with the strongest solution, with a view to using the least amount of water possible in the process. The result is a solution of 12 to 15 per cent. of sugar, which is about the proportion contained in the beet itself.

A greatly desired invention would be the ability to dry these slivers of sugar-beets so that they might be stored and transported, to avoid the necessity of extracting the sugar where the beets are grown. As it is, the beets are harvested, cut up, and the raw sugar extracted in a factory located in the beet districts of Michigan, Colorado, California, or wherever else they may grow. The season is hardly over two months long and the expensive factories remain idle for the other ten months every year. This is bad practice and far from economical. A great saving would be made if the factories could be centrally located and operated all the year through, and as soon as the drying methods are perfected this should be possible. Many have tried to do this, but without success. I am informed, however, that the art has been achieved, although it has not been brought into general practice as yet. The same holds true of cane-sugar, and I understand the plan is worked out and in operation on a small scale to dry the sugar-cane on the plantations, bale it, and ship it to temperate climates, and there have the sugar extracted from the cane all the year round, while the spent cane is then used for making paper.

The treatment of the beet-sugar solution is very similar to that of the juice of sugar-cane. Slacked

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lime is added to neutralize and precipitate the organic acids that are present, along with the phosphates. This is very necessary, because the presence of the acids in solution would decompose or "crack" the sucrose to glucose and fructose, which are not wanted at all. The lime also precipitates the nitrogenous bodies or proteins and some of the coloring-matter. Then it is run through a filter press to get rid of the lime precipitate and, because sugar does not crystallize out well if heated to a high temperature, the solution of sugar and water is boiled down in vacuum pans. As you reduce the air pressure, the boiling-point is reduced. Carbon dioxide is run through the syrup to get out the lime that remains in solution, and after filtration the syrup is still further concentrated until crystals begin to appear. Then it is cooled and the brown sugar crystallized out. This is separated in a centrifugal machine and the molasses, which will not crystallize—is molasses. The molasses, except that which covers buckwheat cakes and goes into gingerbread and candy, is sold for the production of alcohol. Most of the denatured alcohol made in the United States at present is the product of molasses.

Thus we have brown, or raw, sugar. It is dissolved again and filtered through bone-black to remove the coloring-matter. The filtered solution is then concentrated once more in vacuum pans and run into tanks, in which it crystallizes out in the form of granulated sugar, the sugar of commerce. It still has a brownish or yellowish tinge, and we users of sugar in our coffee and tea want the product *perfectly pure*, or, in other words, pure white. Now we can crystallize sugar again and again and it will still have a little yellowish tinge, because that is its natural color. So Mr. Refiner meets the situation by putting a little blue

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coloring-matter into the solution, which neutralizes its yellowish tint. He uses ultramarine, which does us no harm. Then the sugar has a beautiful bluish white color which satisfies us and satisfies him and enables the grocer to make a profit on his high-grade wares.

Sucrose, or cane-sugar, melts at  $160^{\circ}$  centigrade. When kept at its melting-point for a time and then allowed to cool it solidifies into an amber-colored mass that is called in England "barley-sugar," because barley-water was at one time generally used in its preparation. In the United States it is more likely to be called "stick candy," or, going back a generation, "Jackson balls." When cane-sugar is boiled with dilute acids and so is split into dextrose and levulose it will not crystallize readily. That is the reason why a little vinegar (acetic acid) is added to candy that is to be pulled.

*Candy.*—The making of candy is an industry based in part on the fact that sugar becomes "barley-sugar" and is amorphous and glass-like when heated to  $160^{\circ}$  centigrade. When it is heated to  $210^{\circ}$  centigrade it loses water and becomes caramel. It is an important industry when we consider the vast amounts that are exported to tropical countries. The greatest amount is made in the form of hard candies, which are 70 per cent. glucose and the rest sucrose and water. Now let us stop right here and fuss and fume a little over the good people who fear glucose because it is "a chemical product." Let us see how much more of a chemical glucose is than cane-sugar. The glucose is made from corn and the solution is treated with a mild acid to split off the simple sugar from the starch. The cane-sugar is extracted from cane or beets and the solution treated with an alkali to remove the organic acids. This is the chief difference in the processes,

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and if, so far as manufacture goes, glucose is a dangerous chemical while sucrose or cane-sugar is not, then we might as well come to the conclusion that caustic lime is edible while vinegar is a poison. After that, the processes are somewhat similar except that there is no artificial coloring-matter in glucose when it comes upon the market, whereas there is an infinitesimal amount in sucrose, or sugar. The absurd value of the advertising slogan "no chemicals used" is not a favorable comment on our intelligence. It is only one step in advance of the old patent-medicine advertisements that were assured to be harmless because they were "purely vegetable" — and so contained nothing stronger than 40 per cent. of alcohol, or a little morphine, strychnine, belladonna, and such other "purely vegetable" simples. The superstition that anything with a chemical name is dangerous to health is based on crass ignorance. Glucose is just as healthy as sucrose. Years and years of human experience and physiological experimentation prove this.

To return to hard candies, the mixture of glucose, sucrose, and water is heated in open steam-jacketed kettles and then boiled down in vacuum pans to prevent the formation of caramel, while the excess water is removed. Here the flavor and coloring-matter are put in at the end of the process. Then it is run into flat pans on a table, layers of different colors are imposed one upon another, and it is drawn or rolled up and worked into the forms and shapes that are wanted.

Gum goods are chiefly glucose and water with very little cane-sugar. Gum-drops may contain a little gum-arabic, and are molded, dried, put in a pan, and covered with a crystallizing syrup which is a solution of about 50 per cent. sucrose in water. The syrup

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is drained off and sugar crystals form on the outside of the gum-drops.

Peanut-brittle is glucose and cane-sugar heated until the point is reached where it begins to caramelize. Then the peanuts are added. Some makers add roasted peanuts and some prefer unroasted nuts. The syrup is so hot that it cooks them, anyway. Then the mixture is poured upon marble slabs and allowed to cool.

*Chocolate cream-drops.*—The “cream,” or inside, is cane or beet sugar, for they are the same, and water heated together into a creamy consistency, and then it is molded and dried. The chocolate coating contains about 65 per cent. cane-sugar and about 32 per cent. cocoa. To get the right consistency, cocoa butter is added and then the candy is dipped. Machine-dipped candy goes through much faster than that dipped by hand, and so the coating is thinner. Too much of the coating would stick to the machine if it were operated slowly enough to make a thick covering. There is considerable art in making a good chocolate coating. It should have a good cracking quality and break with a snap. If it is not well made it lacks this quality. The dipping mass is better if it is made and cooled and allowed to stand for a few days and then melted for the dipping process. The temperature must also be guarded carefully, because if the mass is too hot the covering becomes streaky.

Chocolate is made by roasting cocoa beans and pressing out some of the oil which is known as cocoa butter. What is known as bitter chocolate, or the chocolate sold for cooking purposes, contains about 50 per cent. of the cocoa oil or butter. The (adjective deleted by publisher) stuff known as cocoa powder or breakfast-cocoa is the pulp of the cocoa beans with

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nearly all the oil pressed out. It is, I believe, entirely wholesome to drink and eat in quantity.

Cheap candies are just as wholesome as the expensive product. The principal difference is that the one is worked by machinery, whereas the other is worked by hand, and the chocolate coverings are much thicker in the more expensive kinds. Poisonous dyes are not used in coloring them; but even if those of questionable effect were employed, cases of poisoning would be more likely to occur as a result of taking too much sugar than from the pigment. The amount of pigment employed is very, very slight.

*Chewing-gum.*—Why Americans chew gum is a fair question to bring up before a debating society. It is said that some 200,000,000 people chew betel-nut, but they are not of the Indo-European races to which we belong. Europeans do not seem to take to gum, although there is a rumor to the effect that the long, silent watches in the trenches have started the habit among many soldiers. For the exercise of the great American jaw no less than 7,000,000 pounds of chicle are imported annually into the United States.

Spruce gum was the secret joy of our childhood, although the amount produced was not large. An apothecary named Colgan, of Louisville, Kentucky, made spruce gum and found a considerable market for his product. He read in one of his trade papers that a large consignment of a gum called chicle made of the sap of the sapota tree had arrived in New York and that the consignees were trying to find a market for it. It had been hoped that it would serve as a substitute for caoutchouc, but this was not successful. So the Louisville man sent for a sample order, tried it out, found that it succeeded, and speculated on all,

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or nearly all, of the cargo with signal success. So the great jaw-wagging began.

Chicle is related to the rubbers, and some of its constituents are the same. The gum-makers melt it in kettles to destroy the fibers and eliminate the water, although they do not heat to a high temperature. It should then be filtered to clean it, although this is not always done. Then glucose is added until it reaches the proper consistency, and cane-sugar and flavoring are stirred in until thoroughly mixed. It is then taken out of the kettle and kneaded into cakes of about twenty pounds each and run through sizing-rolls to bring it into sheets of the desired thickness. Then it is run through scoring-rolls which mark out each piece. Then it is cooled, broken into the pieces marked by the scoring-rolls, and wrapped and marketed.

Cheaper gums are made in whole or part of deresinified Pontianak rubber, and in some it is possible that rubber resins are used. What is needed in the industry is to provide that the gums remain soft in cold weather and to prevent them from growing brittle with age.

*Gums and Varnishes.*—Gums are mostly high sugars—polymerized sugars with molecules of a great many atoms. The more frequently found and consequently cheaper ones have an acid reaction which may come from impurities. They are built up within the tree or plant, which, within its remarkable chemical works, brings water and carbon dioxide into combination as sugars, and bunches the sugars into gums and starch and into cellulose for the walls of its cells.

Of course these gums are legion in number. The cheapest of all is rosin, and some of the most expensive ones are fossilized, the latter making excellent var-

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nishes, but usually hard to dissolve, and a good part of them—about 16 per cent. in practice—is lost by heat when they are dissolved in oils.

The business of a varnish is to make a covering for objects as though it were covered with liquid glass. Paint does similar work except that the covering is opaque, and the differences between paint and varnish are not very clearly drawn; especially since varnishes that are to stand the weather are often loaded up with finely divided lampblack or other pigment. But we need not bother about that. For the present we have to do with varnishes made of gums of one sort or another which we desire to dissolve and apply.

Rosin will not do alone for varnish, because it is too soft; it has no lasting qualities; nevertheless, it is used in some varnishes. Shellac, from the lac tree, is often used in spirit varnishes for inside work, but it is not an ideal covering, either, because it is too waxy. There are trade troubles about it, too. It is graded according to color, which means that it is submitted to all sorts of chemical bleaching agents which often play hob with its chemical structure. General tests of shellac will show not less than 5 per cent. of rosin and vast amounts of rosin are exported from Savannah to East India only to be brought back mixed with shellac. The best of all gums for varnish are copal and fossil resins dissolved with good petroleum benzine and mixed with cold, pressed linseed-oil.

There are two kinds of varnish—spirit and oil. Spirit varnish is usually shellac dissolved in alcohol, and is good for inside work. The point with spirit varnishes is to get the coat on and have it ready for almost immediate use, and when the varnish is once applied we have no further use for the solvent; we



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want it to hie away as quickly as possible and not remain as a boarder. For this purpose many different kinds of solvents are used. There are grain alcohol and wood alcohol, acetone—which makes the varnish thicken too fast—and turpentine and petroleum benzine, as well as others. The automobile business has spoiled the quality of petroleum benzine as we have already noted, because instead of providing a series of light hydrocarbons they now sell a body of the same specific gravity but composed of still lighter petroleums, together with those much heavier. A petroleum benzine supposed to boil at from  $70^{\circ}$  to  $120^{\circ}$  centigrade will contain bodies that distil over at from  $120^{\circ}$  to  $200^{\circ}$  centigrade, and by the time varnish dissolved in that kind of solvent is thoroughly dry your patience is likely to be lost and your temper in trouble.

Fat or oil varnishes are mixed with an oil which leaves a residue that dries slowly as it oxidizes. To assist in this process, “driers” are put in, which are oxidizing agents, such as lead oxide or manganese dioxide. The action is not simple at all.

Linseed-oil is about the best, but the merits of others are urged. Formerly linseed-oil was pressed cold, which produced a splendid product, but the yield was small. Now in order to improve the yield in bad years it is pressed hot, and that brings with it foots and albuminous substances, mucilage, plant tissue, and all sorts of things that are not wanted. The supply of flaxseed is subject to great variations, being large one year and small the next, so while the demand is steady, the rule that “the higher the price the lower the quality” may nearly be said to hold good. The Dutch artists of Rembrandt’s time who made their own pigments were very particular in regard to

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their linseed-oil, allowing it to stand many years in order to get thoroughly clear. Our current methods of the purchase and sale of package goods has resulted in unfortunate ignorance on the part of the artists of to-day of the materials they use. Sir Joshua Reynolds and his colleagues were great hands at trying experiments, and their pictures tell the story.

China-wood or Tung oil is an excellent product of great elasticity, but it is hard to dry. It has a remarkable trick of jellifying after it has been heated and growing insoluble so that it cannot be cut. Its difficulties, however, are being mastered. Soya-bean oil in regard to a medium for paints and varnishes is less understood than linseed or Tung. It is also hard to dry. Cotton-seed oil and corn-oil are often mixed with linseed. They have their uses. Generally speaking, the ultimate use determines how varnishes should be made, although a lot of the chemistry of the art is still unknown.

Spar varnish was originally intended for the wooden spars of ships, and it is a covering designed to stand the worst kind of weather conditions. It is usually a slow-drying oil varnish with good hard gum. China-wood oil is generally used in spar varnishes.

As an instance of the need of varnishes and paints, steel begins to decay as soon as it leaves the rolls. Air, moisture, and sulphur fumes bring this about, so it needs to be covered as soon as possible. The final covering should be with three coats, and it is well to have them of different colors so as to be sure all three coats have been put on. Painters, like other men, have been known to skip work sometimes, and if the same color is used this will not show. But as the pigments are likely to be different metallic oxides or salts, there is also the danger that with different colored paints

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electrolytic action may set up between the different metals and thus hasten the decay of the steel. This world is certainly full of troubles and we need chemical advice at every step!

*Starch.*—These carbohydrates, including the sweet, gummy products ranging from glycerin to the most complex sugars, have ways of bunching up their molecules, sometimes giving up water and sometimes taking it on, and forming a long series of bodies that are of enormous importance in natural processes, but there has not been reached a sufficiently clear agreement and understanding on the subject to bring it into popular discussion. The trained organic chemist, too, can see these molecules in his mind's eye; can be convinced at which point each atom or radical is placed, while we have not wandered sufficiently far in this book to make that problem easy. So we shall only consider the subject superficially.

We know that dextrose, a simple sugar, is easily converted into dextrine, and dextrine, with water, is a gummy substance. Now starch, which is  $(C_6H_{10}O_5)_x$ —that is,  $C_6H_{10}O_5$  multiplied by an indefinite number—is converted by heat into dextrine, and the hot iron of the laundries does this to the starch on linen, covering the fibers with a hardened gum. But the laundry, while the most familiar, is in effect the least use for starch. It is the great assimilation product of plants. The seeds contain it, and this feeds the young plant until it grows big enough to make the carbohydrates—that is, the sugars and gums as well as starch and cellulose which it needs in the process of living and growth, from water and carbon dioxide from the air. It is likely that the plants produce sugars of one sort or another first and then bunch the molecules to gums and starch. We find starch in the following

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percentages in well-known grains: Winter wheat, 63.7; spring wheat, 65.8; barley, 63.5; English oats, 49.7; corn, 64.6; rye, 61.8, and Carolina rice (husked), 77.6. We must have starch in food for both man and beast, as well as for plants. We cannot build up sugars into starch, as nature does, but we can split them down to simpler substances—which nature does also. For instance, dilute acids split starch down to dextrine and then to dextrose or glucose. Heat does this also. In the presence of certain ferments, such as saliva or the diastase of malt, starch is changed to maltose.

Starch is a colloid, not exactly soluble in cold water, and yet in hot water it absorbs so much that it swells up into a pasty mass. This is why rice swells up so when it is boiled. It dries out into minute granules of different sizes—from 0.004 to 0.0079 of an inch in diameter—and in shape according to its origin. Some granules are round, some oval, and some truncated. Whether prepared from corn (maize), as in the United States, or potatoes, as in Europe, or arrowroot, as in the West Indies, the process consists in destroying the cell tissues, usually by mechanical means, and then washing out the starch and drying it carefully. By further treatment with a dilute acid and by heating it is converted into glucose, or grape or corn sugar.

There is another polyose—now you remember the chemical names of all the sugars end in *ose*, so starch is a polyose, or many-sugar—called glycogen, which is found in animal organisms and is usually prepared from the liver. It has the same formula as starch,  $C_6H_{10}O_5$ , multiplied we do not know how many times, and this is a white powder which dissolves in water, giving an opalescent solution. And these glycogens show differences according to the animal from which

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they are isolated. For instance, horse meat may be recognized by its glycogen content, which is greater than that of beef.

The baking of a loaf of bread is a very interesting process, and recent events have proved that it is well worth the chemist's attention. Flour is principally starch in one of its many forms, with some sugars, and then some other bodies. As every baker knows, flour is tricky stuff and full of ways that are vain. There is great room for chemical research in the milling industry, and in baking and cooking, too.

The ingredients for bread are flour and water, yeast, salt, fat, sugar, and milk. Yeast is a member of a considerable family of plants, of which each variety has ways of its own. You can bake bread with brewers' yeast, but distillers' is better, and specially grown yeast for baking is better still. In some countries it is forbidden to use brewers' yeast for baking. When the dough is made it is set aside in a warm place to let the yeast grow, and as this microscopic plant proceeds to do so it produces, as it matures, two bodies which straightway come into use. The first changes the sugar that is within the wheat and that which has been added into a form that will ferment. The second ferments the sugar—that is, it splits it down to ethyl alcohol,  $C_2H_5OH$ , and carbon dioxide,  $CO_2$ . Then the bread rises, because the  $CO_2$  needs room for itself in that solid dough, and it expands wherever it is formed in all parts of the bread, making holes for itself because the sticky gluten will not let it out. The baker or the housewife looks at the dough, observes that it has "raised," and then it goes into the oven.

Here it meets a new situation. In all that heat the alcohol is quickly turned to vapor, and it wants to escape. So does the carbonic-acid gas. In this, espe-

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cially the alcohol appears to succeed, for I have yet to learn of anybody who was made drunk by eating bread. On the outside of the loaf the sugar, by means of the heat and the air, is converted into caramel, and so the crust has an entirely different taste from that of the bread. The yeast is baked, too, but that does no harm—it has finished its business.

Now let us see how chemical research enters into so familiar a process as bread-baking. We shall consider two improvements, both worked out in the Mellon Institute of Industrial Research of the University of Pittsburgh after a start at the University of Kansas, and both by the same man. When the late Robert Kennedy Duncan established industrial fellowships at the University of Kansas, the National Association of Master Bakers wanted to know how to make "salt-risin' bread." This was a product of the frontier, where yeast was not to be had. Some forgotten woman, with a sense of the reasons why things happen, put sour milk and corn-meal and salt, and possibly something else, together until it proceeded to ferment. This she mixed in the dough batch instead of the yeast which she did not have, and sometimes the result was excellent bread. It was not the same as ordinary bread; the holes were smaller and there were more of them. Old frontiersmen often cried out for "salt-risin' bread"; they wanted it badly, and yet no one alive could be sure of success in baking it, no matter how carefully the recipes were followed. So the bakers' association donated a fellowship, and Professor Duncan put Doctor Kohman at work at it. Sometimes he succeeded, and often he failed, until he discovered the bacillus that turned the trick, which developed in the sour milk, corn-meal, and salt. Where did it come from? Out of the air! Doctor Kohman

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selected just the right bacillus, made cultures from it, and to-day any good baker can make salt-risin' bread by using a culture of this bacillus instead of yeast. The products of fermentation are hydrogen and  $\text{CO}_2$ , instead of alcohol and  $\text{CO}_2$ , and some persons find that they can digest this bread while they cannot digest the ordinary product.

Although other improvements in baking have emanated from the Mellon Institute, I shall mention only one more. This is the discovery of how to make yeast do double work, saving some flour, one-half the sugar needed, and producing a better bread. The problem that Doctor Kohman put to himself was whether the yeast, after it had finished its work, had done the best it could. It feeds on the very things contained in the flour, so that it would seem to have all the advantages that growing yeast should have. Right here, I think, we can note the way scientific training causes a man's mind to work. Here was yeast growing in its "natural surroundings," growing just the way it has always grown. The unscientific mind would hardly have gone much further than to look for the best cultures of yeast and the best flour. Now let us follow the chemical twist. Doctor Kohman noted that the ashes of yeast contain a considerable amount of calcium and other metals, and careful determinations confirmed quantitatively what he already knew qualitatively—that the nitrogen content of yeast is high. There is some lime and some nitrogenous protein in flour, but the question followed naturally whether the yeast, that needs considerable lime and fixed nitrogen, can get all it needs from the flour and milk. So he tried the simple experiment of feeding the yeast in the dough batch just enough of what it needs in the form of sal ammoniac or ammonium chloride

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( $\text{NH}_4\text{Cl}$ ) and calcium chloride ( $\text{CaCl}_2$ ) mixed with enough flour to keep them dry in the packages in which they are sold. The process is patented in accordance with the stipulations of the Mellon Institute fellowships, which give control of the rights to the donors, but the public comes into the advantages with better bread all around.

Just to show what the potential value is of a simple invention of this sort, I did a little guessing with Doctor Kohman. First we imagined all the bread in the country to be baked with the yeast properly fed as I have described. Then we guessed 80,000,000 barrels of flour to be baked into bread annually, and we proceeded to figure on the savings. That would be about 160,000,000 pounds of sugar, at, say, six cents a pound, and 80,000,000 pounds of yeast, worth, say, \$16,000,500. This is a little matter of over \$25,000,000 a year. But if we leave this item out of consideration or give the inventor a slice of it and the owners of the patents a hunk of it, we shall still have better, more wholesome, and more nutritious bread.



## XXIV

### CELLULOSE AND NITROGEN COMPOUNDS

The Universal Need of Starch—Baking Bread—What Really Happens—Improvements in Baking—Cellulose—The Chemistry of It—Nitrocellulose—Artificial Silk—Permanent Paper—Fermentation Again—Paper—What It Is—Pulp—Sulphite Pulp—The Waste Liquor Nuisance—The Manufacture of Paper—The Future in Regard to Paper—A Note on Nitrogen Compounds, including Proteins

**C**ELLULOSE.—Here we have another polyose, same formula as starch ( $C_6H_{10}O_5$ )<sub>x</sub>, but just as different from starch as can be. Whether the multiple of  $C_6H_{10}O_5$  is greater or less for cellulose than for starch does not seem to be clear. Naegeli claimed that by treating starch with saliva, salt solutions, and dilute acids (which is what we do to it in the process of digestion) he found two substances—granulose, which was soluble, and cellulose, which was not. If Naegeli was right, then cellulose is a division product of starch—but it doesn't seem established yet. In fact, it looks as though Naegeli was wrong. Cellulose is a very sturdy compound, much sturdier than starch. You can nitrify cellulose just as you can glycerin, and make nitrocellulose, an explosive compound known as guncotton, for cotton is nearly pure cellulose. If you attempt to do this to starch it is apt to split it right down to sugars. Mixed nitric and sulphuric acids dissolve cellulose to nitrocellulose.

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Very strong alkalies will also dissolve it, and so will carbon bisulphide. A solution of mononitrocellulose with alcohol and ether is called collodion. When the solvent evaporates it leaves an elastic skin. The trinitrocellulose looks like fibers of cotton if made from that material. When dissolved in acetone or ethyl acetate and the solvent is removed, it is used for smokeless powder. Artificial silk is made by dissolving trinitrocellulose in alcohol and ether and passing the solution through very fine holes in glass at a pressure of about 600 pounds per square inch. The filaments are received in water which takes up the solvent, leaving a very fine thread which, when ten or twenty are spun together, make a thread capable of being woven. This, however, would make a guncotton gown, because these fibers are of nitrocellulose, and wrought into a gown they certainly would not do for ladies who smoke cigarettes. So, before being spun or woven, the threads are treated with calcium sulphide, which takes over the nitro radicals from the nitrocellulose, leaving pure cellulose, which is just what is wanted.

The use of cellulose is increasing by leaps and bounds. It is the stuff which constitutes the walls of the minute cells of all vegetable life. It may be spun into threads and woven into cloth or felted into paper. It may be made soluble and resolved into the finest threads, and these again rendered insoluble and woven into fabrics of any thickness desired. Cellulose is a generic name; there are many different kinds of it and there is still much to be learned about the structure of its molecules. Nitrocellulose and camphor make celluloid, and if acetic acid, which is another solvent for it, were only cheaper, acetyl-cellulose would take the place of nitrocellulose, as we have noted before, and the fire hazard of moving-pictures and other

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celluloid objects would be removed. Lately Dr. Wallace G. Cohoe has invented a permanent paper for documents consisting of a finely woven cotton cloth covered with a thin film of cellulose. This should be good for five hundred years. The process is patented.

Stable and firm as cellulose is, it has one weakness, and when this trouble once begins its days are numbered. It can, by oxidation, go over to oxycellulose, which is its oxidation product. This is an utterly worthless, amorphous powder, the flour-like stuff that is the product of very old newspapers that crumble to dust in your hand. It may be produced chemically by overnitrifying cellulose until the whole thing is oxidized. The nitro radicals are lost in the process. But nature can also start it going, especially in paper but also in cloth, and once cellulose begins to turn to oxycellulose it goes right on. We shall come to this again in the discussion of paper.

Now let us return to alcohols once more, and especially to ethyl or grain alcohol, which seems to be nature's favorite. We have a close relation here between the alcohols, sugars, gums, starch, and cellulose. While we cannot polymerize or bunch together the sugar molecules until we have starch, you may recall that by heat and pressure and chemical assiduity certain artificial gums have been prepared. But we can split down the starches and cellulose so that we get simple sugars by means of a mild acid. Then, instead of doing the rest ourselves, we call in the yeast plant, of which there are many varieties, and, as we mentioned under the head of bread, the yeast cell contains two specific bodies, one of which oozes out of the cell and converts certain unfermentable sugars into those that will ferment. The difference between unfermentable and fermentable sugar is that the latter

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will ooze into the yeast cell, where it meets another enzyme, as these catalytic bodies are called in organic chemistry, and this second enzyme splits the sugar into alcohol and carbon dioxide. The sugars that lack this osmotic power to penetrate the yeast cells are the unfermentable sugars. Now why will some sugars in solution penetrate that membrane while others will not? An easy guess would be that monoses, or sugars of which the molecules are composed of a single carbon chain, would slip through more easily than those of two or more carbon chains. The only trouble is, it isn't so. Some monoses are fermentable, while others are not, and some of more than one carbon chain are found to be fermentable. We shall have to let the question go unanswered; but I should like to call your attention right here to a great field of chemistry that we can only note in passing, and that is biological chemistry. Questions of fermentation are questions of but one branch of biological chemistry. There are innumerable bacilli that turn the most unexpected tricks for us, such, for instance, as those found in the nodules of leguminous plants that combine nitrogen of the air with some sap within the plant. There are thousands of different varieties of bacilli, each of which produces a certain chemical effect under given conditions, and here is where the biological chemist, usually supposed to be working on problems of physiology, is beginning to be called for in the industrial research laboratory. Many a difficult reaction is accomplished by letting just the right bacillus do your work for you. This is likely to be one of the next great fields to develop—the biological chemist in industry.

PAPER.—The structural base of vegetable fibers is cellulose. The walls of the cells are built of it;

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indeed, cotton is nearly pure cellulose. It is the microscopic, internal framework of wood; that part of it which is not sap or gum or lignin. And it is the substance of paper. Paper is composed of little filaments of cellulose, matted or felted together. Since cellulose is the framework of cells, and everything that has life is made up of them, we should be able to make paper out of a great many different raw materials. But while the industry is a chemical one, the knowledge of cellulose and of its many varieties is still very limited.

For centuries paper consisted of the fibers obtained by the disintegration of linen and cotton rags, held together and given a smooth surface by admixtures of starch, glue, clay, and similar loading and surfacing materials. With increased demand for paper other vegetable fibers came into use. In this way wood pulp was introduced. For a long time only mechanical pulp was known, and this is produced by tearing the fibers of soft wood asunder, grinding diagonally the edges of the natural logs with a stone in the presence of water. These particles contain a large part of the gums and other substances of the tree which are less stable than cellulose. They oxidize on long exposure, and oxidation, whether slow as in this instance, or rapid as with fire, is likely to be contagious; and when the whole paper is transformed to oxycellulose it becomes worthless. As we noted a few pages back, oxycellulose is an amorphous powder with no mechanical qualities whatever.

Mechanical wood pulp was formerly mixed with that made of rags, to its cheapening and detriment; and the rule holds good to this day that the more of this mechanical pulp a paper contains the poorer

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is its quality. Later a Philadelphia chemist named Tilghman made an important discovery. He observed that sulphurous acid has a disintegrating action upon wood, setting the cellulose fibers free from incrusting substances, and this gave a great impetus to the paper industry. The usual method is to treat chips of wood, hacked out so as to give a good length of fiber, with bisulphite of soda, and the sulphurous acid which is set free dissolves all the organic substances except the cellulose. It takes place under heat and pressure. This is sulphite pulp, after it has been treated with water to separate the fibers and bleached. To make a good newspaper requires about 20 per cent. of this product, along with the mechanical pulp.

A stronger quality of sulphite pulp is made by the Mitscherlich process, in which a weaker acid is used. This points the way to improvements in the art, such as the lately developed kraft paper—a very strong wrapping-paper made originally of undercooked pulp. It has also developed what is known as the sulphate process, which, owing to its milder treatment of the wood, is finding increased application.

We should note right here that sulphite-pulp mills have been a great nuisance, because of their waste liquors. That sulphurous-acid solution contains everything in the tree except the cellulose, and it pollutes streams, kills fish, and it takes a long-suffering public and easy-going lawmakers to stand that sort of thing. Modern methods of dehydration bring the solute down to a powder which bids fair to have many uses. There has also been discovered a curious yeast plant that thrives in a sulphurous-acid solution. By means of this the waste liquors are treated so as to produce about 1 per cent. of alcohol, and the production of ethyl (or grain) alcohol from this source is increasing

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rapidly. So is the impatience of the public with the waste-liquor nuisance of those sulphite-mills which do not treat their liquors.

The first process in paper-making is to put the pulp into a tub called a beater, in which, with a great deal of water, the pulp is made to revolve around a center, or "teased," as the expression is, to get the fibers softened. The quality of paper to be made is determined in the beater. Then clay is added to about 15 per cent. of the weight of the pulp, of which about 5 per cent. is retained in the final product, and then red coloring-matter is put in to overcome the yellow tinge of the wood, after which blue is added to make it nearer white.

After coloring, some milk of rosin is thrown in. This is ordinary rosin emulsified with soda ash, and is called engine sizing. In the cheaper grades very little rosin is used. This is followed by alum, which distributes the rosin, but why it does so is more than I can answer. Let us say that it is for some colloidal reason and hurry along to the next subject. All the time the fibers have been in constant motion, and when a thorough mixing has been reached the bottom of the tub is opened and the mass drops down into what is called a staff chest. This is a large box agitated with a paddle into which water constantly pours. From here it is pumped up to the paper-machine floor, where it is first refined in what is called a Jordan, which is constructed like a meat-chopper, and again it is screened, with water pouring over it all the time. It takes about one thousand gallons of water to make one pound of paper. Then, as a thin, milky fluid, it is run into the flow-box of the machine. This is a long table of wire screen, through which the water flows as the fibers are distributed upon it. The

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screens are about sixty feet long and from sixty to two hundred inches wide. By very cleverly devised joggling motions of the screens, which move very rapidly, the fibers are so laid that the paper has, in effect, a warp and a woof. From the screen the paper is picked up and passed through drying-rolls, where the rosin becomes more evenly distributed. If the paper is to be sized, it is passed through a trough of glue. It is then reeled and cut.

Thus the art of making paper is further advanced than the science of it. To furnish the United States with paper requires the trees growing on several million acres every year, and not only is there not enough spruce, balsam, fir, hemlock, chestnut, and poplar, but it seems a shame to use the forests up this way. If these woods were cut and the wood plantations maintained according to enlightened forestry, no harm would be done, although less paper would be made. But we do not do things that way on a large scale in this country as yet. We cut and slash through any old way that will pay best, and that is sometimes very bad for the land and the people. I do not know how to keep up our paper supply and conserve our forests at the same time, so that my complaint is not much more than a whine, at the best. What is needed is something to take the place of these woods, and not only United States Government chemists, but other men of research, are diligently engaged on the problem.

The first thing to utilize will probably be wood waste. Sawdust has not long enough fiber, but slabs and stumps, branches, and roots will probably be availed of as soon as economical methods are devised. Dr. Arthur D. Little, of Boston, a well-known authority, estimated the daily waste of possible paper in the



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yellow-pine industry alone to be 40,000 tons! The making of kraft paper from slabs and other waste is now rather a matter of engineering and transportation than of research. Some work is in process already. Corn-stalks, rice and flax straw, cotton-stalks, and the wild banana are far from a complete list of other possible sources of pulp supply. A very interesting process well past the theoretical stage is the dehydration of sugar-cane on the plantation and the shipment of dried and baled cane for the sugar to be extracted in temperate climates. We referred to this in discussing the manufacture of sugar. It would not only enable the sugar-works to operate all the year round in temperate climates instead of for a short season when the cane is ripe in the tropics, but it would also make the planters independent of the tropical sugar centrals. The resultant paper is of very fine quality.

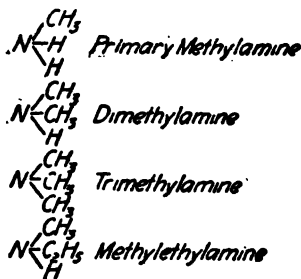
In Europe a grass grown in the southern part of the continent and in northern Africa called esparto is very widely used, and the wild banana of tropical and subtropical America is full of promise. But we haven't got around to it yet, and so far, so long as spruce and other soft woods hold out, they are cheaper.

Aside from the need of new sources of pulp supply, paper-makers would like somebody to invent an improved screen for their Fourdrinier machines. These, upon which the paper is finally made, consist of copper, and copper breaks—the screens are not strong enough. If somebody will be good enough to invent a non-corrosive alloy with great tensile strength that costs no more than copper, the paper-making-machinery people will have something to say to him for his own good.

# EVERYMAN'S CHEMISTRY

## NITROGEN COMPOUNDS

*Amines.*—Ammonia,  $\text{NH}_3$ , has a way of exchanging hydrogen atoms for paraffin radicals, and these are called amines. Without going into details there are combinations of methane,  $\text{CH}_4$ , and ethane,  $\text{C}_2\text{H}_6$ , with ammonia as follows:



In other words, they may be regarded as derivatives of ammonia. The lower members are gases, inflammable, and are very soluble in water. The succeeding members have low boiling-points and are miscible with water. Both they and the lower orders have a characteristic smell, something like boiled lobsters. The higher members are odorless and insoluble in water.

**NITRO COMPOUNDS.**—These contain a  $\text{NO}_2$  group, the nitrogen atom being directly linked to carbon.  $\text{CH}_3\text{NO}_2$  is nitromethane,  $\text{C}_2\text{H}_5\text{NO}_2$  is nitroethane, etc. They have the peculiarity of exchanging one hydrogen atom for an alkali metal, especially sodium. Thus



## CELLULOSE, ETC.

and these sodium compounds are insoluble in absolute alcohol, which gives the chemist the key to their separation.

*Carbylamines.*—Of course the cyanogen,  $C_2N_2$ , radical will turn up, and this it does in two different ways: with the nitrogen atom linked to the alkyl group, as, for instance,  $C_2H_5.NC$ , which is carbylamine or ethyl isocyanide. Another name for the group is isonitriles. They smell to high heaven. The general characteristic is a rank, pungent odor of Simon-pure filth.

*Proteins.*—A possibility, but still an unsolved riddle, is the synthetic production of protein. Protein is a generic name given to those complex bodies consisting of carbon, hydrogen, oxygen, and nitrogen found in both animal and vegetable products which, by the metabolism of the body, are changed into tissue. It is the stuff that makes muscle, and without protein we cannot live. They have molecules of great complexity, and in addition to the elements named they carry sulphur, phosphorus, and other elements. The great Emil Fischer, after clearing up the sugar mysteries and blazing the trail so that nearly every possible sugar is now known, set himself to the task of untangling the protein riddle, and he succeeded in producing, synthetically, certain polypeptides which, had they first been discovered in nature, would surely have been classed as proteins. This is just getting under the edge of the subject, and I think it doubtful if this generation will see the synthetic production of the stuff that meat is made of brought into general practice. On the other hand, it will be interesting to learn, when the European war is over, how much has been accomplished in the way of research to provide synthetic foods in Germany during the blockade. It is possible that necessity may have incited some very

## EVERYMAN'S CHEMISTRY

considerable advances where chemical research has reached so high a stage as it has in that country. They have not, apparently, been able to raise enough vegetable oils to be hardened into the much-needed fats.

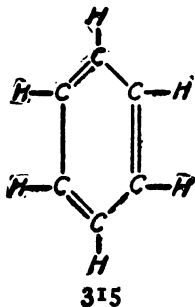
## XXV

### AROMATIC COMPOUNDS

The Benzol Ring—Why These Compounds Are Called Aromatic—  
The Ways of the Benzol Ring—How the Aromatics Are Formed—  
Tar—The Series—Nitrification—Picric Acid—Other Aromatic  
Acids—Positions on the Ring—Higher Aromatic Hydrocarbons

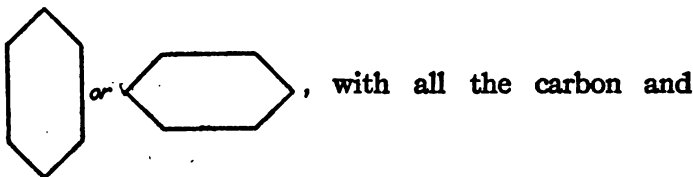
WE must treat in a still slighter manner the other half of organic chemistry, with a view to giving an intimation of the great industries built upon the so-called derivatives of coal-tar.

Substantially all of the products heretofore considered in organic chemistry have consisted of open chains of carbon atoms linked to one another by one and occasionally two and three bonds. Now we come to compounds in which six carbon atoms form the nucleus of the molecule or group of atoms, attached to one another in the form of a hexagon or ring. This is the famous benzol ring which is so often spoken of in chemistry. The formula is  $C_6H_6$ , and it is graphically presented as follows:



## EVERYMAN'S CHEMISTRY

It is often represented as a simple hexagon,



hydrogen atoms supposed to be present except where a substitution is made, as, for instance, in chlorbenzol,  $C_6H_5Cl$ ,



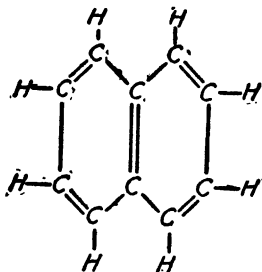
It acts somewhat like an atom with six bonds attached to hydrogen, except for the fact that a few compounds are known in which a carbon atom is replaced by that of another element, but, generally speaking, that ring of six carbons holds tight together. The substitutions take the places of the hydrogen atoms. Benzol,  $C_6H_6$ , is also spelled benzene, and is not to be confounded with petroleum benzine, which is a solvent composed of aliphatic hydrocarbons and is generally lighter than gasoline.

There are fashions and styles in all things from bonnets to coffins, and there are fashions and styles in chemistry, even in chemical names. The termination "ene" for the primary bodies of the aromatic group, such as benzene, toluene, xylene, etc., seems to be in greater favor now than "ol." Being somewhat of an old foggy myself, my pen is likely to slip into habits

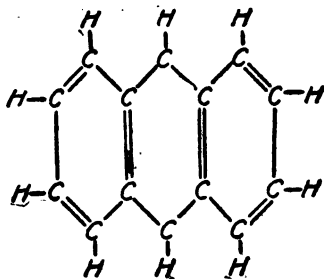
## AROMATIC COMPOUNDS

of expression familiar to my youth and to write frequently of benzol, etc.

These benzol rings are also known in double compounds, in naphthalene,  $C_{10}H_8$ , or



and triplet, as in anthracene,  $C_{14}H_{10}$ , or



Now if these carbon atoms are in groups of six, they must have a certain form, the molecules must have length, breadth, and thickness instead of being geometric planes. But we shall not enter into that problem; the ring is easily imagined and it serves its purpose.

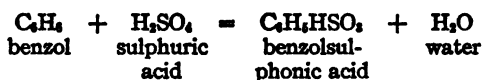
The name aromatic came about through the discovery that certain vegetable substances such as oil

## EVERYMAN'S CHEMISTRY

of bitter almonds, cumin, vanilla, etc., contained much less hydrogen in proportion to the carbon than fatty bodies with the same number of carbon atoms in the molecule. It was also discovered that these compounds built themselves up about the benzol ring. So the name held, although all benzol derivatives are no more odorous than is so-called "butter of antimony,"  $\text{SbCl}_3$ , a butter, or the "sugar of lead" (acetate of lead), a sugar. It is just a name, and the aromatic compounds are those that contain benzol as the nucleus, while the paraffins or aliphatic bodies might be said to be derivatives of methane,  $\text{CH}_4$ .

We shall have to skip so much in order to get at a hasty consideration of dyestuffs and the like that you must take all sorts of things for granted. Please accept the statement, for instance, that there are aromatic acids and ethers and esters and aldehydes and ketones, just as there are aliphatic bodies of this type.

We may, however, consider a few tricks of this benzene ring just as a reminder that we are in a different field from that of the carbon chains. The saturated hydrocarbons of the paraffins are not attacked by concentrated acids, and oxidizing agents affect them only slightly. The benzol ring, on the other hand, is not so robust in this respect. It is neither an acid nor a base, but when attacked by sulphuric acid, for instance, the resultant bodies are another acid and water. The acid is called benzolsulphonic acid, and in the making of this one oxygen atom of the sulphuric acid goes with one of its own hydrogen atoms and one from the benzene ring to produce  $\text{H}_2\text{O}$ . Here is the reaction:





## AROMATIC COMPOUNDS

Nitric acid,  $\text{HNO}_3$ , will do the same thing, leaving a  $\text{NO}_2$  group attached to the molecule.

When vapors of the aliphatic compounds or carbon chains are passed through a red-hot tube, aromatic substances are among the products. Heat and pressure, in the absence of air, induce the production of aromatic compounds. And Nature produces them in her own quiet way, as she pleases.

When coal is heated in iron retorts, raised to red heat, the gas goes out with other vapors while coke remains behind in the retorts. Just what all the bodies were that were in the coal before it was destroyed by distillation nobody knows; it is one of the chemical nuts not yet cracked. The reason is that as soon as you begin to heat it the bodies change, and so we know what is produced by the distillation, but we do not know how these atoms were matched up in molecules before. We know it was not pure coal, because we get so many hydrocarbons and so much ammonia from it.

The first product is a gas, mainly carbon monoxide,  $\text{CO}$ , and with it goes some unsaturated hydrocarbons, some cyanogen,  $\text{C}_2\text{N}_2$ , some sulphur dioxide, and also some of the lighter aromatic bodies such as benzol, toluol, and xylol.

The gas liquor which comes from washing the gas with water contains chiefly ammonia. The next goes by the generic name of tar, and this is what we have to do with now, while

*Coke* remains behind, which is approximately, but by no means wholly, pure carbon.

The tar is distilled again and we have as products:

1. Light oil.
2. Middle oil.
3. Heavy oil.
4. Refined tar.
5. Pitch.

## EVERYMAN'S CHEMISTRY

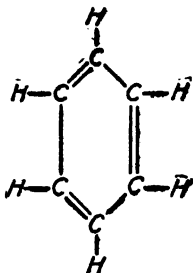
The light oil contains benzol, toluol, the second of the group, and xylol, the third member, and some of the heavier bodies.

The middle and heavy oils contain the heavier members of the aromatic group.

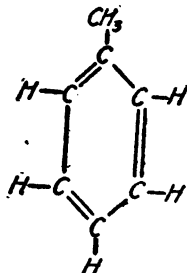
Refined tar contains pitch with the heaviest bodies, and pitch is pitch. It is used for roofing, and lately a method has been discovered and patented for converting it into coke. This was no little triumph, for European chemists have been trying to do this for many years.

Pitch is one of those by-products for which the tar-distillers have long sought in vain a good use. Roofing, etc., takes up only a very small fraction of that which is produced. So to turn it into coke is a great achievement, provided always the discovery pans out well. So far as I know it is not yet in operation on a large scale, therefore the pitch problem is still a problem—at least with most coal-tar distillers.

Now just as methane is the starting-point for the aliphatic compounds, so benzol is the starting-point in this series. From  $\frac{1}{2}$  to 1 per cent. of coal-tar is benzol and toluol, and there is more benzol than toluol found. Toluol is benzol with one hydrogen atom replaced by a methyl group:



benzol



toluol

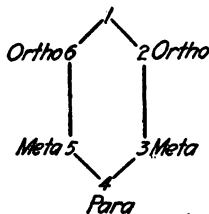
## AROMATIC COMPOUNDS

The third is xylol,  $C_6H_4(CH_3)_2$ , and so the substitutions of H atoms in the benzol molecule continue. Here are a few of them:

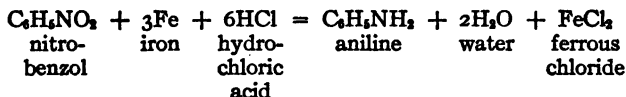
Benzol or benzene,	$C_6H_6$	Boils at	$80.4^\circ$
Toluol or toluene,	$C_6H_5CH_3$	" "	$110^\circ$
Xylene,	$C_6H_4(CH_3)_2$	" "	$139^\circ$
Mesitylene,	$C_6H_3(CH_3)_3$	" "	$164^\circ$

Then we have ethylbenzene,  $C_6H_5C_2H_5$ , and innumerable others.

Just as we can nitrify benzol and make nitrobenzol, so we can add nitro radicals not only to benzol, but to toluol and the other members of the series. They are heavy, oily, and some of them are solid. It makes a difference just where the substitute bodies go upon the ring. In making nitrotoluol, *e.g.*, let us say the methyl or  $CH_3$  group is at point No. 1. Then if the  $NO_2$  attaches itself at point 2 or upon the shoulder it is ortho-nitrotoluol. If at point 4 or at the foot it is para-nitrotoluol, and if at point 3 or at the knee it is meta-nitrotoluol. If a nitro body or  $NO_2$  is attached to all these places it is trinitrotoluol or trinitrotoluene,  $CH_3.C_6H_2.(NO_2)_3$ , and this is the famous T.N.T. used by the armies in siege-guns.



If nitrobenzol is reduced by means of iron filings and muriatic acid, we have the reaction

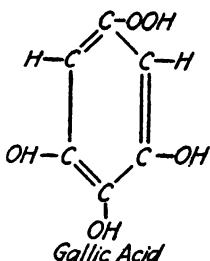


Aniline is the starting-point for many dyestuffs, but let us put off consideration of these for the present.

## EVERYMAN'S CHEMISTRY

Starting with phenol or carbolic acid,  $C_6H_5OH$ , let us proceed to nitrify it with mixed nitric and sulphuric acids. Then we shall finally have trinitrophenol, or picric acid, which is at once a yellow dyestuff and an explosive. Left by itself, however, it will not explode, and if it is dissolved in a test-tube in hot water and allowed to cool, the long, spear-like, yellow crystals form in a beautiful manner. It is a very pretty chemical show.

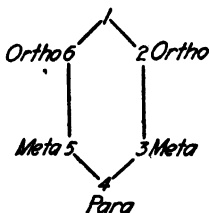
If we start with benzol again, and add  $COOH$  to make benzoic acid, and then substitute  $OH$  for three



more hydrogens, we have gallic acid, which is found in gall-nuts, tea, "divi-divi," and many plants. Closely allied to this are the tannins, or tannic acids, which are very widely distributed in the vegetable kingdom. Tannin is a bitter astringent used in tanning leather and in medicine. In making leather the

hide is saturated with tannin because without it it soon dries to a hard, horn-like substance which, when moist, becomes rotten. Tannin renders it pliant and permanent.

The benzol ring is as whimsical as an Irish lass. Note again, please, the three positions, ortho, meta, and para.

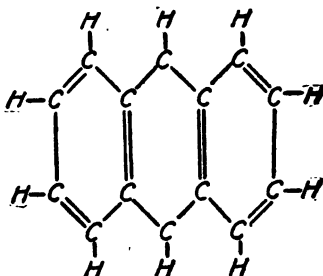
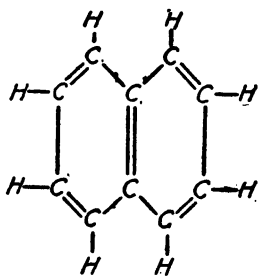


Now whether a body attaches itself to the ortho or para positions may be partially but not wholly controlled by temperature and pressure, while the meta position is likely to be taken up after the other two are occupied, but not always, by any means. Positions 4 and 5, which are also

## AROMATIC COMPOUNDS

respectively meta and ortho positions, may, and again may not, let some radical attach itself in the place of the hydrogen. It requires all the trickiness of an ambulance-chasing lawyer to negotiate some of the aromatic combinations. You can make mononitrotoluol, binitrotoluol, and trinitrotoluol if you please, but as soon as you have three  $\text{NO}_2$  groups attached if you attempt to nitrify it any more you oxidize the whole thing. This trickiness of the benzol ring is why it takes so many chemical specialists, for instance, in the dyestuff industry, and it explains why the explosives-works need such great research laboratories. There are rules, but they are so many and so conflicting that it requires intense familiarity with the individual bodies to be able to change them as desired.

We noted that there were higher hydrocarbons in coal-tar that came over more especially with the heavy oil. These were coupled and tripled benzol molecules, known as naphthalene,  $\text{C}_{10}\text{H}_8$ , and anthracene,  $\text{C}_{14}\text{H}_{10}$ , both of them solids at ordinary temperatures.



Naphthalene is the white, crystalline substance used for moth-balls, while anthracene, of which coal-tar contains less than it does of naphthalene, crystallizes in bluish leaflets. Both are largely used in making dyes.

## EVERYMAN'S CHEMISTRY

The chemical philosophy of dyestuffs is not at all simple. If they were a series of bodies of one kind like the paraffins, the fatty acids, the alcohols, or even the sugars, the problems would be easier to explain. Of course there is a reason for these tinctorial qualities, but it takes a keen vision, a large, catholic sense of the reactions of organic chemistry, to see them, and even then I may add that the Great Tinctorial Principle is not very clearly defined.

There are three general orders of compounds which we have to deal with in this industry which is closely be-cousined with that of making explosives, many photographic chemicals, synthetic perfumery, a large number of medicines, and all sorts of other things. These three orders are, respectively, crudes, which involve the products distilled from tar, such as benzol, toluol, carbolic acid, naphthalene, and the like which come from the coal-tar distillers; the second are known as intermediates, of which you shall soon learn; and the third are the finished products. These industries overlap more or less, but they are distinct, and each one is full of problems of its own. In regard to finished products, no one establishment has ever been able to cover the entire ground, and the same might be said of the intermediates if the term were not so indefinite. The reactions are very subtle, and a great deal of specializing is called for. The industries are remarkably interdependent, and I think it will soon become clear to you why "we"—which means the chemical industry of America—cannot proceed to put up a few shacks and turn out all the dyestuffs there are by a mere resolution to do so. There are about two thousand different synthetic dyes known, but all that we shall do will be to indicate a few of the leading intermediates and then tell something of

## AROMATIC COMPOUNDS

several important colors. All that we shall try to do is to lift the lid, just a little, to show the kind of procedure involved in this field of applied chemistry.

Let us begin by mentioning a few intermediates which are made from the crudes, while the dyestuffs are made from the intermediates.

## XXVI

### COAL-TAR INTERMEDIATES AND FINISHED PRODUCTS

Aniline and Other Intermediates—Colors—Vat Dyes—Position of Dyestuff Industry in the United States—Position of Chemical Industry in the United States—Good-by

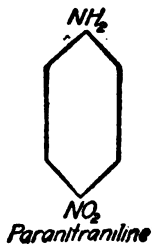
**A**NILINE, as we have noted before, is benzol with one  $\text{NH}_2$  group in the place of one of its hydrogen

atoms.



Paranitraniline is aniline with an  $\text{NO}_2$  group in the

para position





## COAL-TAR AND FINISHED PRODUCTS

Toluidine is toluol.  $C_6H_5CH_3$ , with the  $NH_2$  group

attached.



Phenol is carbolic acid or benzol with an OH group,

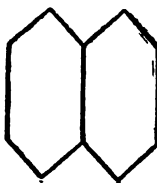
$C_6H_5OH$ .



This is found in tar and is also

made synthetically, starting with benzol.

Naphthalene,  $C_{10}H_8$ ,

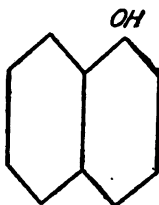


is rather

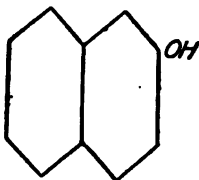
a crude, such as benzol, and naphthol is like carbolic acid, except that we start with naphthalene instead of benzene. The two bodies with the OH radical in two different positions are needed for dif-

## EVERYMAN'S CHEMISTRY

ferent purposes. In alpha naphthol the OH group is in the alpha or first position,



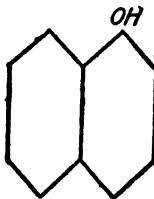
In beta naphthol the OH group is in the second or beta position,



If you remember that phenol or carbolic acid is



and naphthol is



it would

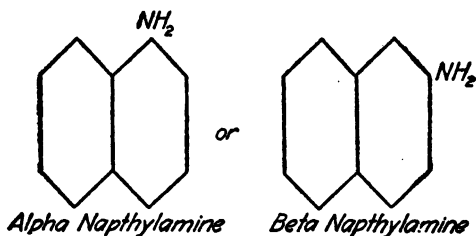
appear that the naphthols should be good disinfectants, and you would be right. Here I throw in with the price of the book a recipe for one of the best hair tonics and dandruff cures: One-half of one per cent.

## COAL-TAR AND FINISHED PRODUCTS

of beta naphthol dissolved in alcohol. If the scalp is dry, dissolve a little castor-oil in it and make it as oily as you need.

Beta naphthol has a slight odor, but is a remarkable deodorant. The naphtholes are made by fusing naphthalene sulphonic acids with caustic soda.

Alpha and beta naphthylamine correspond to alpha and beta naphtholes with  $\text{NH}_2$  in the place of  $\text{OH}$ , and may be compared chemically with aniline, naphthylamine being described as



whereas aniline is

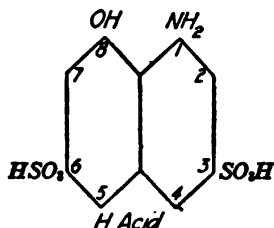


I do not know whether

naphthylamines are poisonous or not, but they smell badly enough to keep everybody away from them that has no business with them.

H acid, so called, is 1—8—3—6, amidonaphtholdi-sulphonic acid.

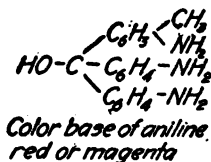
## EVERYMAN'S CHEMISTRY



This is very difficult to make until you know just how, and then it is easy. I only know of two concerns that are producing it successfully in the United States at the time of this writing. Before the book is printed others may be making it.

Aniline was first obtained by the dry distillation of indigo, from which it derives its name, the Spanish word for indigo being *anil*. It is a colorless liquid, oily, peculiar smelling, and boils at 183° centigrade. It has an odd kind of poisonous effect: if a small quantity of aniline is spilled upon the clothing or the skin, it is readily absorbed, the lips turn blue, the skin white, and a general collapse follows. The dyes made from aniline have not these effects; men may work in them and be smeared with them continually with no ill effects.

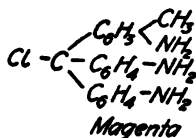
If we bring together three molecules of toluidine and aniline and oxidize them with arsenic acid or nitrobenzol, we get a combination as follows:



which is the color base of aniline red or magenta or fuchsine as it is sometimes called.

## COAL-TAR AND FINISHED PRODUCTS

The chloride of this color base,



is magenta itself.

As we substitute a phenyl group, as benzol less one hydrogen atom is called ( $\text{C}_6\text{H}_5$ ) into the places of hydrogen atoms in the red, we get aniline blue; the more phenyl groups the more greenish the blue.

**AZO COLORS.**—There is a series known as “azo” compounds of benzol of which the simplest would be  $\text{C}_6\text{H}_5\text{.N}\equiv\text{N.C}_6\text{H}_5$ . These two nitrogen atoms in the molecule behave like a central hinge and give the name *diazo* to compounds of which the  $\text{C}_6\text{H}_5\text{N}_2$  group forms a part. This diazonium group behaves something like the ammonium radical  $-\text{NH}_4$  in its habits of combination. Generally speaking, the azo colors are obtained by treating diazonium chlorides with aromatic amines or with phenols. The simplest azo dyes are yellow. Then, as alkyl or phenyl groups (paraffins or aromatic bodies) are introduced into the molecule and the molecule increases in weight, they change from yellow to orange and so on through red, violet, and blue.

Do you catch a little whiff of something that smells like a law here? The more we phenylated (*i.e.*, added  $\text{C}_6\text{H}_5$  radicals to) the rosaniline the more it turned from magenta through violet to a pure cerulean quality of clear blue. The same tendency holds with these azo colors.

Azo colors are not soluble in water, but are soluble

## EVERYMAN'S CHEMISTRY

in alcohol, so the usual practice is to treat them with concentrated sulphuric acid, thus making the sulphonic-acid conjugations, as in aniline blue, and then neutralize with soda. Then they are soluble.

Now let us take a rest for a minute and get a breath of fresh air. We have been trying to treat of coal-tar intermediates in an offhand way, and I'll admit that my conscience pricks me a little. The subject is interesting, I assure you, but we have gone too fast. The trouble is, the only way to slow down would be to make the discourse longer, and that is just what we have not the opportunity to do within the space of this book. The problems are complex, the names are long, and the formulas are bewildering save to those who devote their lives to them. I have only indicated a very few of the hundreds of intermediates, and indicated the way over to a couple of color systems, to show you what is meant by them. Now let us address ourselves to some of the best known colors and see if we cannot achieve greater simplicity in the effort.

Black is the most important color, and of this there are several.

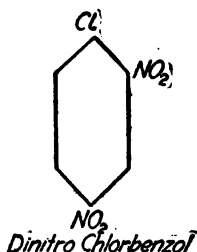
Aniline black is produced by the oxidation of aniline upon the fiber of the goods. The usual method is to produce first what is called aniline salt by treating aniline with hydrochloric acid, and after treating the fiber with this to oxidize it with chlorate of potash and other oxidizing agents. This is the old aniline black that replaced logwood.

Nigrosine is made by heating aniline salt with nitrobenzol until a pasty mass is formed which is dropped into water. It is then sulphonated and neutralized (to make it soluble) and dried and ground. This is the black of shoe-blackening, stove-polish, etc.

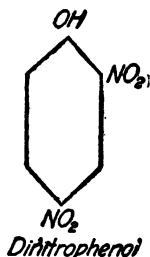
Sulphur black. This involves the process of making

## COAL-TAR AND FINISHED PRODUCTS

sulphur colors, and just what the reactions are it would be hard to say. You may gather an armful of dried leaves and boil them up in a kettle with sulphide of sodium and sulphur, and a brownish vat-dye will result. So by treating other materials with sulphide of soda and sulphur you get dull browns and yellows and blues and greens and a good black. They are very fast against washing, but not very fast against light. The largest use is for black cotton stockings. To make this black we must first produce an intermediate which we have not yet described. We start with benzol, treat it with chlorine, and make chlorbenzol,  $C_6H_5Cl$ . This is nitrified by means of nitric and sulphuric acids until we have dinitrochlorbenzol. Let's make the picture:

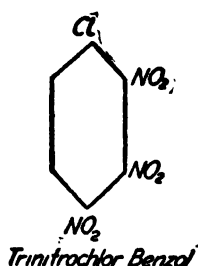


Now let us boil this with soda ash (sodium carbonate) and the chlorine will be removed and an OH group goes on in the place of it. This gives us dinitrophenol, or

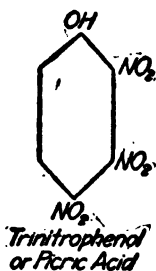


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By heating this with sodium sulphide and sulphur we get the required sulphur black for socks. But note, please, how the cousinship between dye-stuffs and explosives may be found right here. One method of making picric acid—indeed, the method generally in vogue in England—is to follow this same process, but go one step further in the nitrification, so that trinitrochlorbenzol is produced.



Then oxidize this to



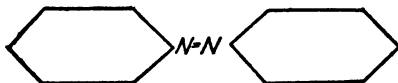
and we have trinitrophenol, or picric acid.

Erie Black, or Direct Black, is the best black there is. It was developed at the Schoellkopf works in Buffalo, and nothing from any other country is equal to it. It is made from H acid, benzidine, meta-

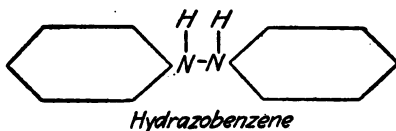


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phenylendiamine, and aniline. Benzidine is a curious thing. If you start with azobenzene, which is



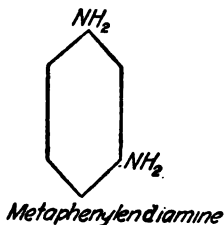
or two benzene groups hinged together by two nitrogen atoms, and treat this with zinc dust and alcoholic potash, you get hydrazobenzene, or



Now if you treat this with a strong acid, those two benzene rings will turn somersaults, joining apparently by their other ends or else the groups of NH will go to the ends, where they will find another hydrogen atom:



I assure you, there never lived a chemist yet who knew all of the devious ways of that benzene ring! Metaphenyldiamine is not so bad as it looks. It is aniline with another  $\text{NH}_2$  group in the meta position—



I do not know what the

## EVERYMAN'S CHEMISTRY

reactions are that produce Erie black; they are very complicated.

The black for wool and silk which is most generally used is called alpha-naphthylamine black. It is made by coupling alpha-naphthylamine, which you may remember is like aniline except that it starts with naphthalene instead of benzol and has the  $\text{NH}_2$  group in the first, or alpha, position, coupled with what is known as Freund's acid; which is like H acid except that it has a hydrogen atom in the place of the OH group. This is shaded with other colors.

Of reds the most widely used is called para red,

being made from paranitraniline. This



is diaz-

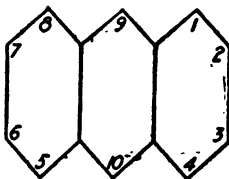
otized with sodium nitrite ( $\text{NaNO}_2$ ) and mixed with beta naphthol. The coupling takes place immediately, and the red dyestuff separates out. This red is used on bandana handkerchiefs and other cheap cottons; it is the red of wagon paint and fire-engines, barn doors, and wherever a fiery red is wanted. The consumption of it is enormous. It is the great cheap red, and has replaced Turkey red or madder or alizarine (all the same) where cheapness rather than quality is wanted. It is not by any means as good a color for cotton goods as alizarine.

The old aniline red or magenta to which we referred a few pages back is also called fuchsine, from fuchsia, and it is used on print cloths and elsewhere.

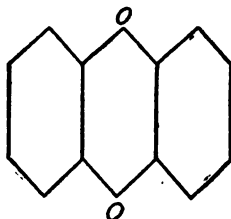
## COAL-TAR AND FINISHED PRODUCTS

There are also a whole series of azo reds used as scarlets.

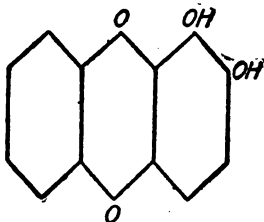
Turkey red is a product of anthracene,  $C_{14}H_{10}$ :



The first step is to oxidize it by sodium dichromate and sulphuric acid, which leaves an oxygen atom at positions 9 and 10 and has the formula  $C_{14}H_8O_2$ :



This is now treated with oleum or fuming sulphuric acid containing 50 per cent. sulphur trioxide. This forms a sulphonic acid, and when the whole is fused with caustic soda in the presence of chlorate of potash, the  $SO_3$  group is removed and alizarine is formed. This is  $C_{14}H_8O_2(OH)_2$ , or



*Alizarine*

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This is the real old Turkey red, formerly produced from the madder plant and replaced by this discovery of Graebe and Liebermann, away back at the beginning of the 'seventies. Alizarine is almost insoluble in water, and is only slightly soluble in alcohol. Its value as a dye consists in its power to form, with metallic oxides, fine colored, insoluble compounds called "lakes." When cotton is mordanted with one of these oxides it can be dyed with alizarine and the color depends upon the oxide used. With ferric oxide it is a violet black, with chromium oxide claret color, with calcium oxide blue, and with tin and aluminium oxides it produces the various shades of Turkey red.

There are certain colors, some of which are made with alizarine as a base and some are not. They belong chiefly to the azo group and are reduction colors or vat-dyes, being first reduced and then oxidized on the fiber. They are the fastest cotton colors known, and include the lighter shades of reds, yellows, blues, and greens. The principal use is for shirtings and the like. They are referred to as the indanthrene group and by other names chosen by different makers. Most of them are still patented.

In blues the anilines are still used, as is methylene blue, but larger use is found for the H acid as benzo sky-blue. In this H acid is coupled with dianisidine, a very complex body, by simple coupling, and the blue dyestuff separates out. It is especially used on silk and cotton.

Indigo is a romance. The antiquity of its use is shown in the fact that many mummy-cloths are dyed with it. It was introduced into Europe in 1516, and bitter was the fight against the "devilish drug" which was declared to spoil fabrics and work all kinds of injury by the growers of woad, the rival blue of those

## COAL-TAR AND FINISHED PRODUCTS

days. In 1737 its use was graciously permitted in France, and after that the other nations followed suit.

Natural indigo is produced from a great series of leguminous plants grown in India, China, and Egypt, the Philippines, and tropical South America and Africa. Over 10,000,000 pounds of the dyestuff is used annually in the United States alone. With untiring patience the great A. von Baeyer worked over the problems, then others contributed one idea after another, and when it was found that the start might be made with naphthalene and aniline the Badische Anilin und Soda Fabrik began to build. Before the first pound of artificial indigo was brought upon the market in 1897 the Badische works had expended over \$5,000,000. By 1911 it had driven the use of natural indigo practically from the face of the earth, from China and India as well as from Europe and America. The artificial is the same as the natural, but purer and more reliable.

We shall not enter into the process, which is very complex and has to do with a considerable number of catalytic agents. It requires vast quantities of coal-tar products—of sulphuric anhydrid ( $\text{SO}_3$ ), a great deal of mercury, of chlorine, of ammonia, and of caustic soda.

It is a vat-dye—that is, one in which an insoluble pigment is treated with an alkaline reducing agent whereby it becomes soluble in the alkaline bath. As such it is absorbed by the fabric which is dipped into it. Then it is oxidized by exposure to the air and is thus reconverted into the insoluble pigment again, but now thoroughly absorbed by the fibers.

To get an idea of the situation in this country, let's hark back to the dyestuff census that was printed after much gnashing of teeth by the United States

## EVERYMAN'S CHEMISTRY

Government in 1916. It contained a list of all the dyes imported in 1913. There were a great many repetitions in it because different makers had different names for similar products. Then, too, different dyes were often mixed together in Germany to attain certain shades, and new names applied to the mixtures. The use of special labels for different customers was also a frequent practice among dealers and agents.

Before the war there were five concerns making synthetic dyestuffs in the United States. Now, aside from twenty-three concerns producing crudes (and these do not include the retort coke-oven plants or phenol makers), and sixty-eight makers of the intermediate materials, there are ninety-eight concerns making finished dyes. They are not wholly devoted to making these products; some began to make certain specialties otherwise unobtainable for their own use, and now they produce for the market; others confine themselves to one or two colors, and still others are only starting up. On the other hand, some are vast concerns, working intensely with rare talent and skill and rapidly enlarging their capacity and variety of product.

Roughly speaking, 75 per cent. of the dyestuffs needed are made in this country and of this three-quarters some are made in such excess that a considerable export trade is carried on to friendly countries, especially to England. Of others there is a shortage, and this is serious in such basic colors as magenta, methylene blue, auramine, methyl violet, and a few more. The prices of many of them are away up in the air, which has lured into the business a number of minor concerns in which the art is lacking to secure adequate yields. Some also are under incomplete chemical control and fail to purify their materials

## COAL-TAR AND FINISHED PRODUCTS

properly. This is incidental to pressing need and hasty establishment which the whip of time will correct. On the other hand, the very highest praise should be awarded to the conscientious manufacturers who have strained every nerve to meet the country's needs, often at the expense of profit.

We have, then, three-quarters of the dyestuffs needed, some a-plenty and others scarce. In regard to quality, American-made dyes are the same as German dyes, only there are not so many of them. If some small makers are still short in their yields, the loss is theirs. If they do not purify their materials enough, the defect is more likely to be in shade than in fastness. This is a complete catalogue of the defects of American-made dyes and it does not apply to the products of the important makers. Nevertheless, dyers have been sorely put to it. They have had to use one material when they wanted another, and the substitutions have often been unhappy. They have also been compelled to relearn the art of using dye-woods for many purposes which are new to the present generation, and this is not to be learned in a day. The trouble, however, has principally come from the makeshift substitution of wrong materials for the right ones, because the right ones are lacking. The colors themselves are the standard articles whether made in Germany, France, Switzerland, England, or here. And missing and scarce products are coming upon the market as agreeable surprises at short intervals.

In regard to the missing quarter, Congress cut off from the tariff bill the *ad valorem* duty on indigo and alizarine products, which discouraged manufacturers at the start. Nevertheless, indigo is now being made by the Dow Chemical Company at Midland, Michigan, although at present there is not enough made

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and natural indigo imported to meet even the needs of the United States Navy. But the National Aniline & Chemical Works, Inc. is building a great indigo plant, and it is generally understood that the Du Pont Chemical Company is about to begin, so that with these great concerns engaged in it, the production of all the indigo we need is only a question of time. In chemical research they are the peers of the great German establishments.

Alizarine colors are lacking. There is Turkey red for bandana handkerchiefs, towels, and print goods, and alizarine blue, employed in connection with indigo for navy blues and on serges, dress goods, and suitings. Although these are not produced yet, the crude body from which they are made, anthracene, is now available, and one or two of the largest makers have the matter in hand. It is merely a question of time and organization.

Fast cotton vat-dyes of the indanthrene type are also missing, but the research laboratories are busy and the outlook is hopeful. A good wool black of the "Diamond" type is needed. Logwood is now used in the place of it, and this is not fast enough against light. There is also a shortage of safranines and the general class of azine colors, including azo carmine for red and pink on silk and for printing, which a large print works in New England is beginning to make. Besides these, there is wanted a good developed black of the diamine or diazo type for a rich, full, bloomy black on fine cotton hosiery and cotton-silk goods. These are the chief absentees, but by the time this is printed their number may be less.

That is the situation at the end of three years, in August, 1917. The number of colors produced to-day or the number of dyestuffs missing is not the important



## COAL-TAR AND FINISHED PRODUCTS

fact. In 1914 we had neither crudes nor intermediates to speak of. These are now abundant. We then made a bare one-fifth of our needs out of foreign materials; now we make three-quarters of those needed and some for export, all of American materials in American apparatus, and by American chemists. We have the talent, the organizations, the capital, and the will. The men in the business are familiar with the financial side of chemical problems; they also know what chemical research means. The coal-tar product industry is established in this country and it is here to stay. The missing quarter of the dye-stuffs needed will soon be provided and it looks as though only the odds and ends would eventually come from abroad.

Chemical industry in the United States has grown by leaps and bounds, but it lacks co-ordination. The pressure to produce has made all sorts of odd associations in production. I know of a wall-paper manufacturer who is making salicylic acid. He was under the necessity of making some dyes which he could not purchase, and, having some extra room and a live chemical director, he took up this drug as a side line. One of the great pulp and paper companies is making chlorbenzol and carbon tetrachloride from excess of chlorine for bleaching, and also carbon bisulphide—because a demand was found for it. Sulphite-pulp mills are producing alcohol in increasing quantities, and a very large paint-manufacturing firm is one of the leading producers of paranitraniline—because they needed para red and could not buy it. Chemical industry has not yet thoroughly settled down in this country.

It is surely a great deal clearer than mud that the dyestuff industry is only a part of the whole. It is so

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interrelated with others that it cannot be considered as a single unit. By means of splendid organizations and much more intensive scientific application to the task than we or any other folk have been accustomed to, together with the aid of government-owned railways, subsidized steamship lines, the imperial secret service, and laws designed to encourage co-operation among manufacturers, the Germans built up almost a world monopoly of the dyestuff industry. During the three years of war no such machine has been established here. No such perfect machine could be built up under our laws and customs. For instance, in one of the great works in Germany orthonitrotoluol was needed as the starting-point for the manufacture of one of its leading products. Now when toluol is nitrified some of the  $\text{NO}_2$  radicals will take the ortho position and some will go to the para position; but no amount of conniving has enabled chemists so far to make orthonitrotoluol without producing at the same time some paranitrotoluol. The best practice yields these products in the relation of two to one, respectively. It is easy to separate them after they have been made. Now in this particular reaction only the ortho body was useful; there was no use for the para body. What they did with the para body no one knew; even their competitors were uninformed. But when Liège fell the secret was out. The explosive used was TNT, or trinitrotoluol, and if you want to make that you can very well start with paranitrotoluol, because you have it already one-third nitrified. The next  $\text{NO}_2$  group will then take the ortho position, and the third will hook on to the meta position, for all TNT is nitrified in each of the 2, 3, and 4, or ortho, meta, and para positions. So for ten years or more that paranitrotoluol was being quietly shipped

## COAL-TAR AND FINISHED PRODUCTS

to the German government munition-works, made into TNT, and stored against the Day of Wrath.

I do not offer this in praise of German methods. I give the incident merely by way of explaining them.

It would be idle to try to report fully on American chemical industry at this time. It is not sufficiently co-ordinated. And Congress we have always with us, often more vindictive than enlightened. It would be unjust and unfair to say that the Government of the United States is adverse to industry, but I declare it sometimes seems as if, at first sign of any other than a fighting relation between this Government and a successful industry, the desire ripens in Congress to launch a persecution under the name of investigation. We have also had more than a little defective chemical engineering. There has been a rush and a tumble, and a hurry and a scurry, and some men are not up to their jobs. Others again are masters, real giants in mind and understanding, and they are doing things with a big intelligence and with a steady look to the future that give one faith in the days to come. American industry is launched upon a chemical career. This has taken from colleges and universities some of the best teachers, while many young men have resolved to become chemists who should have resolved to become almost anything else, so far as chemical progress is concerned. So we shall not have smooth sailing.

Without doubt many small manufacturers will be crowded out of business when normal times come again and the markets of the world are open; not so much because they are small as because when the scramble is over and prices become competitive their methods will prove to be faulty. On the other hand, the great American concerns have gone into chemistry to stay. The research laboratories of a number of

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large American corporations are marvels of scholarship, thoroughness, and efficiency, and compare favorably with the great German works.

When we think how powerless and how dependent we were upon Germany in 1914 and how by the present year, 1917, American chemists have met thousands of problems that Germans claimed that only they could solve, how panic and distress and closed factories have given way to the industries of peace as well as those of war with merely incidental inconveniences due to the closed German ports, it seems no more than fair to take off our hats to the men who have done these things and to give them their meed of praise.

We must omit discussion of all sorts of interesting subjects, because we have not the space and also because we have not entered into organic chemistry with sufficient thoroughness to do so. If I have allowed my enthusiasm to go further than your interest will follow, I beg your pardon. We are, all of us, poor judges of our own dullness. The main thing is to think you can see these things in your mind's eye; the wandering of atoms and ions or radicals from one molecule to another and shaping themselves up into equilibrium. There is chemistry in nearly everything that happens, and if your chemical sense is aroused everything that takes place becomes much more interesting. And if your curiosity is quickened, I shall count myself fortunate, because then you may follow up the subject, read profound books, watch the rushing sap in growing corn, observe the most marvelous of all chemical processes in nature—the synthesis of sugar from water and  $\text{CO}_2$  in green leaves—and maybe, some day, either you or somebody else will know how it is done.

# APPENDIX I

## THE ELEMENTS

Sym-bols	Names of Elements	Approx. Atomic Wt. and Valence	Boiling-points in Degrees Centigrade	Description
Al	Aluminium	27—3	1800-1	Familiar light metal. Found in clay, feldspar, bauxite; very wide-spread. Melts at 657°.
Sb	Antimony	<sup>3</sup> 120—4 5	1440	Silvery-white solid with metallic luster. Usually found with arsenic, which it resembles in many ways. Melts at 629°.
A	Argon	40—0	- 186	One of the inert gases of the air, of which it forms less than 1 per cent. Makes no combinations.
As	Arsenic	<sup>3</sup> 75—4		Steel-gray, metal-like substance. Poisonous in all its compounds. Sublimes without melting at about 100°.
Ba	Barium	137—2		A metal of the alkaline earths. Something like calcium. Sulphate used as filler for paper and for paint. Melts at 850°.

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Symbols	Names of Elements	Approx. Atomic Wt. and Valence	Boiling-points in Degrees Centigrade	Description
Be	Beryllium	9—2		Silvery metal. Found in Beryl. Rare. Behaves like magnesium. Melts above 960°.
Bi	Bismuth	<sup>3</sup> 20—4 5	1420	Grayish-white solid, lustrous, same family as As and Sb. Melts at 270°.
B	Boron	11—3		Brown powder. Found as boric acid and a borate of sodium or borax. Does not melt. Volatilizes slightly in electric arc.
Br	Bromine	<sup>1</sup> 80—3 5	59	Brown liquid. Volatile. One of the halogens.
Cd	Cadmium	<sup>7</sup> 112—2	780	Metal somewhat like tin and zinc. The yellow sulphite is used as a pigment. Melts at 320°.
Cs	Cæsium	133—1	1670	One of the alkali metals. Very rare. Melts at 26°.
Ca	Calcium	40—2		One of the alkali metals. Lime is calcium oxide. Very widespread. Melts at 780°.
C	Carbon	12—4		Diamond, graphite, coal. Everything having life contains it. Organic chemistry is chemistry of carbon compounds.
Ce	Cerium	140—3		Metal of rare earths.

# APPENDIX I

Symbols	Names of Elements	Approx. Atomic Wt. and Valence	Boiling-points in Degrees Centigrade	Description
		4		Used in gas mantles and for striking sparks on cigar-lighters. Melts at 623°.
Cl	Chlorine	35.5—1	— 33	Greenish gas. Halogen. Very wide-spread in common salt, in rocks everywhere.
Cr	Chromium	52—6	2200	Steel-gray metal used for hardening steel. Salts are used for pigments. Melts at 1520°.
Co	Cobalt	59—3 4		Hard white metal. Very like nickel. Compounds used in pigments. Melts at 1478°.
Cu	Copper	63.5—1 2	2300	Next to iron the metal in greatest use. Melts at 1082°.
Dy	Dysprosium	162.5—3		Hardly known. Found in rare earths.
Er	Erbium	167.5—3		Hardly known. Found in rare earths.
Eu	Europium	152—3		Hardly known. Found in rare earths.
F	Fluorine	19—1	— 187	Greenish-yellow gas. One of the halogens. Found in fluorspar and other rocks.
Gd	Gadolinium	157—3		Hardly known. Found in rare earths.
Ga	Gallium	70—3		Rare metal something like Al.
Ge	Germanium	72—2 4		Very rare metal found sometimes with Ag and Pb.
Au	Gold	197—1 3	2530	Almost more important socially than it is

# EVERYMAN'S CHEMISTRY

Sym-bols	Names of Elements	Approx. Atomic Wt. and Valence	Bolling-points in Degrees Centigrade	Description
He	Helium	4—0	— 27	chemically. Melts at 1064°. Companion of argon. Spectroscope shows it in photosphere of the sun. Also found occluded in rocks.
Ho	Holmium	163.5—0		Hardly known.
H	Hydrogen	1—1	— 152	Lightest gas. Two-thirds by volume of water. The business end of all acids, and, with oxygen, the business end of bases.
In	Indium	115—3		Rare metal. Same group as Ga.
I	Iodine	127—1	184	Violet-black solid. Found in sea-water and marine products. Heaviest of the halogens.
Ir	Iridium	<sup>2</sup> 193—3 7		Grayish - white metal, very like platinum. Melts at about 2000°
Fe	Iron	<sup>2</sup> 56—3	2240	The metal in greatest use. Melts at 1530°.
Kr	Krypton	83—0	— 152	An inert gas of the air present to the extent of 0.00005 volumes in 1,000.
La	Lanthanum	139—3		Another element found in the rare earths.
Pb	Lead	209—2 4	1525	Gray metal usually found as sulphide. Poisonous in all combinations. Widely used. Melts at 326°.
Li	Lithium	7—2	1400	An alkali metal, like



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Sym-bols	Names of Elements	Approx. Atomic Wt. and Valence	Boiling-points in Degrees Centigrade	Description
				sodium and potassium. The lightest of metals. Melts at 186°.
Lu	Lutecium	174—3		Found in rare earths.
Mg	Magnesium	24—2	1120	A very light, silvery metal, that would be largely used for its mechanical qualities if it were cheap enough. Melts at 632°.
		2		
		3		
Mn	Manganese	55—4	1900	A gray metal, harder than iron, used in iron and steel industry. Melts at 1245°.
		6		
		7		
Hg	Mercury	200—1	357	Silvery liquid. Dissolves and forms amalgams with many metals. Solidifies at - 39°.
		2		
		3		
Mo	Molybdenum	96—4		Black metal alloyed with steel to make "high speed" tools. Mo compounds are used in pigments.
		5		
		6		
Nd	Neodymium	144—		Little known of it. Found in rare earths.
Ne	Neon	20—0	- 233	Inert gas of air. 0.015 parts per 1,000 of it in atmosphere.
Ni	Nickel	59—2		Silvery metal, first cousin to cobalt. Used for alloying steel and for nickel-plating. Melts at 1452°.

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Sym-bols	Names of Elements	Approx. Atomic Wt. and Valence	Boiling-points in Degrees Centigrade	Description
Cb	Niobium	<sup>3</sup> 59—5		Rare metal found with tantalum. Formerly called columbium, whence the symbol Cb. Melts at 1720°.
Nt	Niton	222—		Name given to radium emanation.
N	Nitrogen	<sup>14—3</sup> 5	— 194	Gas comprising four-fifths of air. Hard to get into combination, but when this is achieved it becomes very lively.
Os	Osmium	<sup>2</sup> 191—4 6		Like iridium, one of the platinum metals. Melts at about 2300°.
O	Oxygen	16—2	— 182	Gas comprising one-fifth of the air. The old Jupiter Maximus of chemistry.
Pd	Palladium	<sup>2</sup> 106—4 6		Another rare metal of the platinum family. Melts at 1549°.
P	Phosphorus	<sup>31—3</sup> 5	290	Poisonous white waxy substance, very inflammable, and an amorphous brown powder. Widespread in rocks and living things. Melts at 44°.
Pt	Platinum	<sup>2</sup> 195—4 6	2450	Harder than silver or gold. Does not combine easily with oxygen or with acids. Melts at 1753°.
K	Potassium	39—1	700	Alkali metal, whitish, wax-like substance.

# APPENDIX I

Sym- bols	Names of Elements	Approx. Atomic Wt. and Valence	Boiling- points in Degrees Centigrade	Description
Pr	Praseodymium	140—3		Highly inflammable; very wide-spread. Melts at 62°.
Ra	Radium	226—2		Of the rare-earth series. White metal that turns black in air. Exceed- ingly rare, radio-ac- tive. Melts at about 700°.
Rh	Rhodium	103—		A rare metal of the platinum group. Melts at 1650°.
Rb	Rubidium	85—I	696	A rare alkali metal sim- ilar to cæsium. Melts at 38°.
Ru	Ruthenium	102—		A rare metal of the platinum group. Melts at about 2000°.
Sm	Samarium	150—		Of the rare-earth series.
Sc	Scandium	44—3		Very rare. Something like Al.
Se	Selenium	<sup>2</sup> 79—4 6	688	Gray, metal-like, solid, and amorphous brown powder. Found associated with sulphur. Has properties of metal. Conductivity of elec- tricity is increased in the light. Melts at 170-217°.
Si	Silicon	28—4	about 3000	A brown powder and dark - gray crystals. Constitutes one- fourth of the earth. With O it is sand. Melts at 1500°.
Ag	Silver	108—I	about 1350	White metal known since prehistoric times. Conducts

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Sym-bols	Names of Elements	Approx. Atomic Wt. and Valence	Boiling-points in Degrees Centigrade	Description
Na	Sodium	123—1	877	heat and electricity better than copper. Melts at 962°. Alkali metal. Consistency of cheese. Oxidizes on exposure to air. Part of common salt and very wide-spread. Melts at 97°.
Sr	Strontium	87.5—2		One of the alkaline earth metals with calcium and barium. Sr compounds produce red flames; used for Greek fire. Melts at 800°.
S	Sulphur	32—2 4 6	448	Amorphous yellow powder, yellow crystals, brown, solid and other forms. Very wide-spread. Melts at 103°.
Ta	Tantalum	181—4 5		Gray metal found usually with niobium. Used for electric lamp filaments. Melts at about 2850°.
Te	Tellurium	127—2 4	1390	Silver-gray with metallic luster. Similar to selenium. Melts at 453°.
Tb	Terbium	159—0		Metal of the rare earths
Tl	Thallium	204—1 2		Metal, rare, like gallium and indium.
Th	Thorium	232—3 4		Metal of rare earths. Used for incandescent gas mantles with 5 per cent. of cerium. Melting-point very high.

# APPENDIX I

Sym-bols	Names of Elements,	Approx. Atomic Wt. and Valence	Boiling-points in Degrees Centigrade	Description
Tm	Thulium	168—		Metal of the rare earths.
Sn	Tin	118—2 4	2275	Ore widely distributed but not plentiful. One of the very trickiest of metals. Melts at 231°.
Ti	Titanium	2 48—6		Found nearly everywhere in minute quantities. Alloyed with steel to increase toughness. Melts at 1795°.
W	Tungsten	2 4 184—5 6		Like molybdenum. Uses: electric - light filament for the metal and solutions of compounds render cotton and other fabrics slow burning. Melts at about 2450°.
U	Uranium	3 4 238—5 6		Related to molybdenum and tungsten. Compounds are used for making fluorescent glass. Melts at about 1500°.
V	Vanadium	2 51—3 4 5		Silvery metal. Head of vanadium family which includes niobium and tantalum. Increases hardness and malleability of steel. Melts at 1720°.

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Sym- bols	Names of Elements	Approx. Atomic Wt. and Valence	Boiling- points in Degrees Centigrade	Description
X	Xenon	130—0	— 109	Inert gas. 1,000 parts air contain 0.000006 parts X.
Yb	Ytterbium	172—3		Very rare. Same fam- ily as scandium, lan- thanum, and yttri- um. Related to Al.
Y	Yttrium	89—3		See Ytterbium.
Zn	Zinc	65—2	916	Bluish - white metal. Almost as tricky as tin. Melts at 418°.
Zr	Zirconium	90—4		Rare - earth metal. Used with thorium and cerium. Melting- point very high.

In chemical compounds the symbol of an element indicates an atom of it. If there is more than one atom of any one element to be indicated, a small figure at the lower right of the symbol is used.

The valence of an element is the number of bonds or hyphens with which an atom of it is found combined with those of other elements in molecules. This is not usually indicated by any special sign.

A formula indicates a single molecule. Thus a molecule of water is composed of two atoms of hydrogen and one atom of oxygen. It is written  $H_2O$ . Two molecules would be  $2H_2O$ , and five molecules  $5H_2O$ . Since hydrogen is univalent—that is, since it has but one bond or hook or hyphen for combining, the formula shows that oxygen is attached to it in water with two bonds. A more graphic way of writing the formula for water would be  $H-O-H$ .

A chemical equation indicates a chemical process

## APPENDIX I

and shows the changes in molecules. For instance,



means that one molecule of sulphur trioxide combines with one molecule of water to produce one molecule of sulphuric acid.

The metric system of weights and measures is in universal use in scientific work, and unless special mention is made the centigrade thermometer is indicated in all records of temperature. It is easy to change centigrade to Fahrenheit by multiplying the number of degrees centigrade by 1.8 and adding 32. To change Fahrenheit to centigrade, deduct 32 and divide the remainder by 1.8.





## APPENDIX II

### BIBLIOGRAPHY

VERY popular and not at all technical are the delightful books of the late Robert Kennedy Duncan: *The New Knowledge*, published by the A. S. Barnes Company, of New York, and *Some Chemical Problems of Today*, and *The Chemistry of Commerce*, both published by Harper & Brothers. Another excellent book, easy to read and which requires no previous chemical knowledge, is Samuel T. Sadtler's *Chemistry of Familiar Things*, published by J. B. Lippincott & Co., of Philadelphia. Geoffrey Martin's *Triumphs and Wonders of Modern Chemistry*, and his *Modern Chemistry and Its Wonders* (D. Van Nostrand Company, New York), are also interesting. The chemical world is so vast that these popular treatises hardly overlap one another in subject.

I have attempted to go deeper into the chemical aspect of things than is usual in popular books, in the hope that you may be persuaded to go on with the subject after you have had your turn with me. If you do, and want to begin with a short text-book, there is a good one designed for high schools called *Chemistry of Common Things*, by Brownlee, Fuller, Hancock, and Whitsit, four high-school teachers of chemistry, that is very well arranged. Allyn & Bacon, of New York, publish it. It is a good book to start with, but of course it is not comprehensive. If you

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want to get right into the heart of the thing, I recommend *Modern Inorganic Chemistry*, by J. W. Mellor, published by Longmans, Green & Co., New York, or Alexander Smith's *Inorganic Chemistry*, brought out by the Century Company. I could make a much longer list, but these are both good books. In the organic field I like Bernthsen's *Organic Chemistry* (D. Van Nostrand Company, New York) and Lassar-Cohn's *Practical Organic Chemistry* (Macmillan Company). Another good one to start with is *Principles of Organic Chemistry*, by J. F. Norris (McGraw-Hill Book Company). A good introduction to physical chemistry is found in the first volume (Theoretical Part) of *Qualitative Chemical Analysis*, by Julius Stieglitz (Century Company). This leads along into the modern theories of solutions; but while the solutions are usually dilute, the book is rather concentrated. It is a beautiful work, but it was not meant to while away an idle hour. On colloid chemistry there is *Colloids and the Ultra Microscope*, by R. A. Zsigmondy, translated by Jerome Alexander (John Wiley & Sons, New York), and *The Chemistry of Colloids*, by W. W. Taylor (Longmans, Green & Co.). In regard to radium and radio activity, going more profoundly into the subject than did Doctor Duncan in his *New Knowledge*, there are two good works by Ernest Rutherford—one called *Radio Activity*, and published by G. P. Putnam's Sons, and the other *Radio Active Transformation*, bearing the imprint of Charles Scribner's Sons.

The practical man, however, knows very well that he cannot get the whole theory of chemistry into his head by a twist o' the wrist, and he is likely to be anxious to get at the books written on the subjects in which he is already interested with a view to under-

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standing as much as he can. A good general survey of the industrial field may be obtained from Allen Rogers's *Manual of Industrial Chemistry* (Van Nostrand). A new edition will appear about the time the present work is issued. A shorter book is *Industrial Chemistry for Engineering Students*, by H. H. Benson (Macmillan). The following more or less technical works (some being more and others less) are standard:

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